IN ENGLISH TRANSLATION

75th BIRTHDAY OF ACADEMICIAN E. V. BRITSKE

Highly respected and beloved Edgard Viktorovich!

The Division of Chemical Sciences of the Academy of Sciences USSR send you their best wishes on the occasion of your 75th birthday, and of the 50th anniversary of your scientific, pedagogic, and social activities.

It is difficult in this short greeting to enumerate all of your valuable contributions to the development of chemistry and chemical industry in our country. During these many years you have trained a very large number of chemists and engineers, who are now working productively in various branches of science and industry, among whom are to be found a number of academicians, associate academicians, and professors, who are worthily carrying on the work of their teacher.

As one of the active participants in, and organizers of, the Soviet system of scientific research institutes and industrial establishments, you made a great contribution to the industrialization of the Soviet Union, to the creation of its chemical industry, and to the realization of the Stalin Five-Year Plans. From the very beginning of the October Revolution up to the present day you have successfully held leading positions in scientific and scientific-technological organizations, and you worked actively in the Higher Soviet for National Economy and in the National Commissariat for Education. You took part in the creation of the basic chemical and fertilizer industries, and in the construction of a number of factories and mining establishments. You devoted much energy to the organization and management of the Institute of Applied Mineralogy and of the Institute for Fertilizers and Insecto-Fungicides. You were the first Academician-Secretary of the Division of Technical Sciences of the Academy of Sciences USSR, and you were the Vice-President of the All-Union Academy of Sciences. In your capacities, first of Professor of the Riga Polytechnical Institute, and then of the Plekhanov Institute of National Economics, and the Moscow Higher Technological School, you gave leadership to a vast school of industrial chemists. As a member of the All-Union Academy as well as of the V.I. Lenin Academy of Agricultural Sciences, you took part in the planning of research work, thus contributing to the development of the chemical and metallurgical industries and of agriculture.

Your scientific research work in the Institute of Metallurgy of the Academy of Sciences USSR led to the development and introduction into industry of new processes for treatment of minerals.

During the Great Patriotic War you displayed great administrative ability as the Vice-Chairman of the Commission for Mobilization of the Resources of the Urals for the Needs of Defense.

A characteristic feature of your activity is your constant effort towards linking theory with practice, and towards introducing science into industry.

Your extensive researches on the physical chemistry and improvement of methods of treatment of minerals, and towards finding new ways of processing natural phosphates and sulfur, arsenic, fluorine and other ores, and your profound studies of thermal processes and of physico-chemical properties of products, have led to the formulation of a number of theoretical rules applying to metallurgical and technological processes, based on the most recent advances in physical chemistry.

A thermal process for distillation of phosphorus from its ores, with the utilization of the gases and slags produced, was worked out on the basis of your discoveries, as were also a process for the complex treatment of titanomagnetites, and processes for the production of concentrated fertilizers and of arsenical insectofungicides.

The Government has valued your work very highly, awarding you a Stalin Prize, 1st Class, and a number of orders and medals.

The Division of Chemical Sciences of the Academy of Sciences USSR wishes you health, strength and long life, for the continuance of your creative work, which is directed towards the development of Soviet chemistry and technology, and towards the strengthening of the power, prosperity and culture of our great Fatherland.

Division of Chemical Sciences, Academy of Sciences USSR

PERIODIC LAW OF D. I. MENDELEEV AND THE STABILITY OF CO-ORDINATION COMPOUNDS

A. A. Grinberg and K. B. Yatsimirsky

One of us, when compiling the second edition of the monograph "Introduction to the chemistry of co-ordination compounds" [1], in 1950, considered the question of whether any connection exists between the position of an element in Mendeleev's periodic table and its ability to form co-ordination compounds. This study was based on a statistical treatment of the experimental material, and led to the following conclusions:

1. The tendency towards formation of co-ordination compounds is least in elements of Group O, and in elements of the immediately neighboring Sub-groups a of Groups I and VII (possessing the most stable electron shells).

2. The maximum tendency towards co-ordination compound formation is to be found among the elements of Group VIII (having the most labile electron shells, with unfilled d-levels). The elements of groups adjacent to Group VIII, are similar to these; this applies in particular to copper, silver and gold, which Mendeleev considered to be adjacent to the corresponding Group VIII elements, and to a smaller degree to elements of the zinc sub-group and to those of sub-group VII (b).

3. Thus, in the long periods, the capacity for forming co-ordination compounds is seen to be smallest at the margins, and greatest at the center.

4. The same applies basically to the short periods (Li $\longrightarrow$ Ne) and (Na $\longrightarrow$ Ar). The precise localization of the maximum is unlikely to be derivable from a statistical approach.

5. The "vertical" regularity found in the chief sub-groups appears to be that the power of functioning as a central ion is connected with a certain optimum range of values of "tension" of the ionic field. Very small values of this property are associated with an abrupt fall in the tendency towards complex formation. Very high values are associated with increase in the stability of the complexes with certain addenda (F, O), but the diversity of possible addenda is reduced.

It will be evident from the above that within sub-groups Ia and IIa the tendency towards complex formation falls with increasing atomic weight (volume) of the elements, whereas the reverse appears to apply to sub-groups a of Groups VII, VI, V and IV. Group III elements should occupy an intermediate position, which is particularly evident when this sub-group is considered together with the lanthanides.

The vertical regularity found in sub-groups b is less uniform. An important part is here played by the type of electron shell of a given element. It may be said, very generally, that there is a tendency within these sub-groups for complex-forming capacity to increase parallel with the atomic weight (copper, silver, gold; zinc, cadmium, mercury; gallium, indium, thallium; manganese, rhenium). The order in which the elements may be arranged may, however, vary according to the type of complex whose stability is being compared.

The above observations are, of course, only a first approximation to the answer to our problem, but even so they permit of the forecasting of the properties of a number of compounds. Bjerrum [2] attempted in 1950 to classify co-ordination compounds according to their stability in aqueous solution, on the basis of the periodic law, but his work is obviously of only very limited scope. Not only does this author confine his studies of complex-formation to aqueous solution, but he draws no conclusions regarding changes in the stability of the compounds along the periods, and says very little as to the nature of the stability variations within the groups.

It should also be noted that the parallelism noted by Bjerrum between the basic properties of addenda and their capacity for forming co-ordination compounds with ions of metallic elements has long since been pointed out by other authors. However, Chugaev [3] quite rightly said in 1906 that "the basic properties of amino-nitrogen, whether of diamines or of mono-amines, cannot be considered to be the sole factor determining the degree of stability of co-ordination compounds. It is evident that some other factor or group of factors, the nature of which
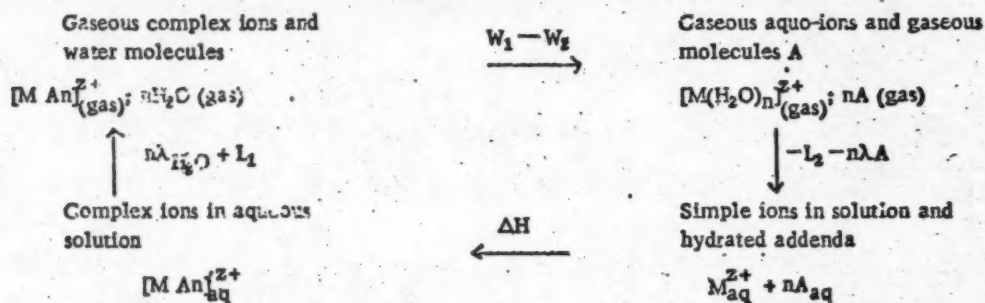
is not yet known, is responsible[a].

We shall in this communication attempt to clarify the connection between the periodic system and the capacity for co-ordination compound formation, based on a quantitative study of this property. The quantitative aspects considered will be the energy of formation of the gaseous complex ions, calculated according to Yatsimirsky's method [4] and also the instability constants.

The former magnitudes characterize the process of complex formation, in its pure form, so to speak. The latter characterize differences between the stability of a given complex ion and its corresponding aquo-ion. However, inasmuch as aqueous solutions represent the most important practical case, although only a particular one, the selection of instability constants as a measure of the stability of the compounds seems to be justified, both from the theoretical and the practical points of view.

The relation between the two parameters selected by us follows from the following considerations. It has been shown by one of us [5] that in reactions of co-ordination compound formation of the same type the change in entropy remains constant. Hence in such cases the heat of formation of a given compound in aqueous solution differs from the change in free energy associated with this process by some constant amount. The heat of formation of the complex in aqueous solution characterizes its stability, and we are justified in using thermochemical cycles for the evaluation of free energy changes.

Let us consider the following thermochemical cycle, for the process of formation of the complex ion $[M An]^{z+}$ from the central ions M^{z+} and $\underline{n}$ addenda A:

Gaseous complex ions and water molecules

$[M An]^{z+}_{(gas)}$; nH_2O (gas)

$\xrightarrow{W_1 - W_2}$

Gaseous aquo-ions and gaseous molecules A

$[M(H_2O)_n]^{z+}_{(gas)}$; nA (gas)

$\uparrow n\lambda_{H_2O} + L_1$

$\downarrow -L_2 - n\lambda A$

Complex ions in aqueous solution

$\xleftarrow{\Delta H}$

Simple ions in solution and hydrated addenda

$[M An]^{z+}_{aq}$

$M^{z+}_{aq} + nA_{aq}$

L_1 and L_2 represent the heats of hydration of the ions $[M An]^{z+}$ and $[M(H_2O)]^{z+}$, respectively, W_2 and W_1 are the "addition energies" [4] of A and H_2O, respectively, to the gaseous ion M^{z+}; λ_{H_2O} is the latent heat of vaporization of water, and λ_A is the heat of hydration of the addendum A.

We obtain by summation of changes in enthalpy in all sections of the cycle

$$\Delta H = (W_1 - W_2) + (L_1 - L_2) + n(\lambda_{H_2O} - \lambda_A). \tag{1}$$

For reactions of the same type the last term is constant, and the penultimate one approximately so, whence

$$\Delta H \approx (W_1 - W_2) + const. \tag{2}$$

Taking into account the constancy of the difference between change in enthalpy and free energy, and the relation between the instability constant and the latter magnitude, we finally obtain the following expression:

$$RT \ln K \approx (W_1 - W_2) + const. \tag{3}$$

This expression shows that a direct connection exists between the instability constant and the energy of formation of gaseous ions. The instability constant is, as a first approximation, equal to the difference between the addition energies.

The experimental values given in Table 1 are in good agreement with those calculated from the expression.

Unfortunately, our quantitative characteristics cannot yet be applied to all elements forming co-ordination compounds, and to all types of compound formed by them. The reason for this is that on the one hand we possess approximately accurate numerical data for the energy of formation of gaseous complex ions for a few cases only (aquo- and amino-ions), and on the other that we possess insufficient data relating to instability constants. Nevertheless, a study of this row has enabled us to arrive at certain quite interesting conclusions, applying in particular to elements of the subordinate sub-groups.

TABLE 1

Relation between energy of addition and the instability constant of complexes
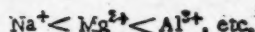
Complex ions	Addition energy in kcal (W_2)	Addition energy for the hexa-aquo complex (W_1)	Difference between addition energies $(W_2 - W_1)$	Free energy of formation of the complex $\Delta Z = RT \ln K$	$W_2 - W_1 + \Delta Z =$ = const
$[Mg(NH_3)_6]^{2+}$	320 [4]	300 [4]	20	4.5 [6]	25
$[Co(NH_2)_6]^{2+}$	359 [4]	324 [4]	35	−7.0 [6]	28
$[Ni(NH_3)_6]^{2+}$	370 [4]	329 [4]	41	−11.9 [6]	29
$[Coen_3]^{2+}$	372 [4]	324 [4]	48	−18.8 [6]	29
$[Nien_3]^{2+}$	383 [4]	383 [4]	54	−25.3 [6]	29
$[Znen]^{3+}$	372 [4]	331 [4]	41	−16.4 [7]	25

We shall now proceed to compare :

(a) ions with an analogous structure of the outer electron shell, but with different charges and radii, and

(b) ions with identical charges, but with different structures of the outer electron shell.

The laws governing tendency towards co-ordination compound formation can readily be deduced for ions possessing an outer electron shell of the inert gas type (2 and 8 electrons); this refers above all to ions actually able to exist in solution, i.e., in general those having a charge of not more than 3^+.

Such ions (in particular, uni- and bi-valent ones) form complexes held together chiefly by electrostatic forces. The stability of the complex is here determined basically by the magnitude of the charge and by the ionic radius. For this reason, the heat of formation of such complexes varies parallel with the charge of the ion, and inversely with its radius

$$Na^+ < Mg^{2+} < Al^{3+}, \text{ etc.}$$

In accordance with the above, the stability of complexes falls with increase in the atomic number (from above down).

TABLE 2

Addition energies for hexa-aquo-ions and hexa-amino-ions of elements of Group II of the Periodic Table

Ions	Addition energies for ions of the types	
	$[M(H_2O)_6]^{2+}$	$[M(NH_3)_6]^{2+}$
Be^{2+}	—	411 [4]
Mg^{2+}	300 [4]	320 [4]
Ca^{2+}	257 [4]	237 [4]
Sr^{2+}	219 [4]	198 [4]
Ba^{2+}	—	171 [4]

The ions of this group do not characteristically form complexes with addenda which chiefly give rise to covalent linkings (Br^-, CNS^-, I^-, S_2O_3, CSN_2H_5 etc.). Complexes with addenda forming "intermediate" type linkings (NH_3, $C_2H_4(NH_2)_2$) are unstable. The ions of sub-groups a of Mendeleev's system yield complexes which are stable in solution, with addenda which are bound to the central ion basically by electrostatic forces (F^-, OH^-, O^{2-}, H_2O). As for ions with an inert gas type of electron shell, the stability of the complexes, in the gaseous state or in solution, rises from left to right in the periods, and falls from above down in the groups, since it depends basically on the charge and the radius of the ions. It may be expected that the stability of complex fluorides and oxy-ions of the higher valency "ions" of the right-hand side of the periodic system (such as F^{5+}, S^{5+}, Cl^{7+}, etc.), which are not encountered in the free state, should also rise from left to right along the periods, the dominating role of electrostatic characteristics being retained. Deviations from the rule may be expected here, however, owing to increase in the role played by covalent bonds as the charge increases.

The relative stability of complexes of this type should also fall from above down in the vertical groups. We emphasize that we are here speaking specifically of ions with an electron shell of the inert gas type, such ions as As^{5+}, Sb^{5+}, etc., are not considered here.

Substantially different rules are found for ions of elements of sub-groups b of Mendeleev's Table, with 18 electrons in their outer shell. Co-ordination compounds with predominatingly electrostatic bonds are not charac-

teristic of this group, within which the binding forces between the central ion and the addenda are typically of a mixed nature. We find here that with the ionic type of bond, stability should diminish down the groups as the atomic number rises, whereas with the covalent type of bond the stability of the complexes should be at a maximum for elements of the 6th period (effect of ionization potential).

As a result of the summation of these oppositely acting factors it is often found that within sub-groups b the heats of formation of the corresponding gaseous ions fall initially, and then rise abruptly (Table 3).

TABLE 3

Addition energies for gaseous ammine-cations formed from elements of sub-groups b.

Complex ions	Addition energies	Complex ions	Addition energies
$[Cu(NH_3)_3]^+$	131 [4]	$[Zn(NH_3)_2]^{2+}$	366 [4]
$[Ag(NH_3)_3]^+$	104 [4]	$[Cd(NH_3)_2]^{2+}$	311 [4]
$[Au(NH_3)_3]^+$	160 [4]	$[Hg(NH_3)_2]^{2+}$	376 [4]

The same observation applies to the free energy of formation of the corresponding complexes in aqueous solution (Table 4).

The more clearly defined is the covalent nature of the bond, the more steeply does the stability of the complex rise, from above down (Table 5).

The data of Table 5 show that, for the case of iodides, the change in free energy of formation of complexes varies very abruptly in a vertical direction, but much less so in the case of chlorides; bromides occupy an intermediate position. It is of interest that increase in the charge of the central ion does not in this case lead to increase in the stability of the complex, but even to its slight diminution, at least in the cases studied (with the exceptions of Au^I and Hg^{II} bromides).

TABLE 4

Change in free energy in formation of complex ions in aqueous solution (ΔZ)

Central ions	Types of complexes					
	$[M(NH_3)_2]^{2+}$	$[M(NH_3)_4]^{2+}$	$[Men_2]^{2+}$	$[M(C_2O_4)_2]^{2-}$	$M(NH_2CH_2CO_2)_3^-$	$MN(CH_2CH_2NH_2)_3^{2+}$
Zn^{2+}	−6.55 [6]	−12.9 [6]	−14.1 [7]	−10.0 [8]	−16.5 [9]	−19.9 [10]
Cd^{2+}	−6.5 [6]	− 9.7 [6]	−13.6 [7]	− 7.9 [8]	−15 [9]	−16.7 [10]
Hg^{2+}	−23.8 [6]	−26.2 [6]	−	−	−	−31.0 [10]

TABLE 5

Change in free energy in formation of halide complexes

Complex ions	$\Delta Z = RT \ln K$	Complex ions	$\Delta Z = RT \ln K$
Chlorides			
$[CuCl_2]^-$	− 7.54 [11]	$[ZnCl_3]^-$	− 0.20 [14]
$[AgCl_2]^-$	− 7.70 [12]	$[CdCl_3]^-$	− 3.70 [15]
		$[HgCl_3]^-$	−19.0 [16]
Bromides			
$[CuBr_2]^-$	− 8.05 [11]	$[ZnBr_3]^-$	1.4 [14]
$[AgBr_3]^{2-}$	−14.0 [13]	$[CdBr_3]^-$	− 4.6 [15]
$[AuBr_2]^-$	−16.9 [11]	$[HgBr_3]^-$	−16.2 [16]
Iodides			
$[CuI_2]^-$	−12.00 [11]	$[ZnI_3]^-$	1.8 [14]
$[AgI_3]^{2-}$	−20.4 [13]	$[CdI_3]^-$	− 6.8 [15]
		$[HgI_3]^{2-}$	−41.3 [11]

Very little material is available relating to the stability of complexes formed from central ions having an 18 + 2 electron shell (Sn^{2+}, Pb^{2+}, Sb^{3+}, Bi^{3+}, etc.). The behavior of these ions in many respects resembles that of 18-electron shell ions, but there are also certain significant differences.

It is of considerable interest to compare the stability of complexes formed from central ions possessing an identical charge. It is here possible to follow the effect of the structure of the outer electron shell on the stability of the complexes, since in this case the radius of the ions remains approximately constant within a period (e.g., Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, or Cr^{3+}, Mn^{3+}, and Fe^{3+}). The stability of complexes in which the ionic type of bond predominates (fluorides, phosphates, sulfates, etc.) is determined by the magnitude of the charge and by the dimensions of the corresponding ions, and

for this reason such complexes are not very typical of uni- and bi-valent ions, but are highly characteristic of ions with charges of 3[+] or more. The stability of complexes having a type of chemical bond approached to the covalent one is determined by the magnitude of the ionization potential [4], which is connected with the structure of the outer electron shell.

The stability of the complexes rises from left to right along the periods (according to the increase in the number of d-electrons) to a maximum, and then falls abruptly, beginning with the element having 10 d-electrons (18-electron ion). The possibility of a fall in the complex-forming capacity of elements before the filling of the 18-electron orbit is not, however, excluded. This may occur when the given ions possess a well-marked oxidative action (Ni^{3+}, Cu^{2+}, Ag^{2+}, etc.). Increase in the redox potential is up to a certain limit associated with increase in the stability of the complex, but above this limit the central ion decomposes the addenda, by oxidizing them.

Table 6 presents changes in free energy associated with formation of a number of complexes of bivalent central ions. In all cases the stability of the complexes rises to Cu^{2+}, and then falls abruptly, starting with Zn^{2+}.

TABLE 6

Change in free energy (ΔZ) in formation of certain complexes in aqueous solution

Type of complex	Central ions					
	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$[M(NH_3)]^{2+}$	—	—	− 2.9 [6]	− 3.70 [6]	− 5.65 [6]	− 3.22 [6]
$[M(NH_3)_4]^{2+}$	—	—	− 7.5 [6]	−10.82 [6]	−17.2 [6]	−12.90 [6]
$[Men]^{2+}$	−3.7 [6]	− 5.8 [6]	− 8.0 [6]	−10.20 [7]	−14.3 [7]	− 7.77 [7]
$[Men_2]^{2+}$	−6.5 [6]	−10.2 [6]	−14.6 [6]	−18.75 [7]	−26.6 [7]	−14.10 [7]
$[Mpn]^{2+}$	—	—	—	−10.1 [7]	−14.4 [7]	− 8.00 [7]
$[Mpn_2]^{2+}$	—	—	—	−18.7 [7]	−26.7 [7]	−16.65 [7]
$[M(C_2O_4)_2]^{2-}$	−7.3 [18]	—	—	—	−14.1 [17]	−10.0 [8]
$MN(CH_2CH_2NH_2)_3^{2+}$	−7.9 [10]	−11.7 [10]	−17.4 [10]	−19.9 [10]	−25.6 [10]	−19.9 [10]

A similar order is found for addition energy, i.e., for the heat of formation of gaseous complex ions from gaseous central ions and addenda (Table 7).

TABLE 7

Addition energy for gaseous ions [4]

Type of complex	Central ions									
	Ca^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$[M(H_2O)_6]^{2+}$	257	—	—	—	288	—	324	329	348	331
$[M(NH_3)_6]^{2+}$	237	—	—	324	314	337	359	370	388	366

The results described above may serve for the prediction of the possibility of existence and the stability of as yet uninvestigated complexes. Thus it may be supposed that the stability of complexes of the type $[M(C_2O_4)_2]^{2-}$, derived from the ions Fe^{2+}, Co^{2+}, and Ni^{2+} should increase from Fe^{2+} to Ni^{2+}, and that the free energy change associated with their formation should be within the limits −7.5 to −14 kcal. It may also be supposed that the addition energy for the hexa-aquo-ions of Ti^{2+}, V^{2+}, and Cr^{2+} should lie within the limits between 260 and 290 kcal, and the addition energies for hexa-ammine ions of Ti^{2+} and V^{2+} should be between 240 and 320 kcal.

The correlation of the stability of complexes with the place of the appropriate elements in the periodic table has thus permitted the formulation of certain generalizations, and the checking of experimental data, as well as the prediction of the stability of as yet unknown complexes.

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THERMOCHEMISTRY AND STRUCTURE OF ATOMS

PART 6. THERMOCHEMISTRY OF BORON: APPLICATION OF THE RULE OF THERMOCHEMICAL LOGARITHMICS TO ELEMENTS OF THE THIRD GROUP OF D. I. MENDELEEV'S SYSTEM

A. F. Kapustinsky and O. Ya. Samoilov

The increasing practical and theoretical importance of the chemistry of boron has attracted the attention of numerous research workers. Direct measurements of the heat of formation of boron oxide have been made, but the values reported by different workers differ considerably from each other. Roth and Borger [1], who combusted boron in oxygen, found that the heat of formation of the vitreous oxide was 349 $\pm$3 kcal, corrected by Roth in 1946 [2] to 339 $\pm$ 2.3 kcal. This value is in close agreement with that reported by Todd and Miller [3], viz., 335 $\pm$ 0.8 kcal, for spectroscopically pure boron. In 1949, however, Eggersgluess, Monroe, and Parker [4] repeated the work on direct measurement of the heat of formation of vitreous B_2O_3, which they found to be 281.1 $\pm$ 3.1 kcal. They ascribed the difference between their result and those of Roth and Borger and of Todd and Miller to contamination of the samples of boron with hydrides of boron.

Johnston, Hersch, and Kerr [5], in a paper devoted chiefly to the determination of the specific heat of elementary boron at low temperatures, derive the heat of formation of crystalline B_2O_3 (302.0 $\pm$ 3.4 kcal) from the summation of the thermal effects of five processes, including the heat of hydrolysis of diborane, which is, according to Roth and Borger [1] equal to 108.1 kcal.

Southard [6] determined the heat of dissolution of vitreous and crystalline B_2O_3 in water at 25° (1000 mole of water per mole of B_2O_3), finding values of 7.82 and 3.46 kcal per mole respectively. The heat of transformation of vitreous into crystalline B_2O_3 is thus 4.36 kcal per mole, according to Southard. According to Artsdalen and Andersen [7] the heat of dissolution of vitreous B_2O_3 in water at 25° (1110 mole of water per mole of B_2O_3) amounts to 7.928 $\pm$ 0.029 kcal per mole, and is only very slightly dependent on the final concentration of the solution. The value for infinite dilution is 7.960 kcal. per mole.

Only one value for the heat of formation of gaseous BCl_3 is known to us, viz., that of Troost and Hautefeuille [8], who in 1870 reported a value of 104 kcal. The heat of hydrolysis of gaseous BCl_3 (910 mole of water per mole of BCl_3) amounts, according to these authors, to 79.2 kcal per mole. Berthelot later found [9] that the heat of hydrolysis of liquid BCl_3 (650 mol of water per mol of BCl_3) at 10° is 65.8 kcal per mole, and that its latent heat of vaporization is 4.5 kcal per mole. According to Berthelot the heat of hydrolysis of gaseous BCl_3 is 70.3 kcal per mole. Roth [2] takes the heat of formation of BCl_3 as being 104 kcal.

We have determined the heat of hydrolysis of gaseous BCl_3, by a method depending on passing the gas through water at 25° in a calorimeter with an insulating envelope. Knowing the heat of hydrolysis of BCl_3 we can calculate from the heat of formation of B_2O_3 the heat of formation of BCl_3. As will be shown below, it is possible from this to arrive at the correct value for the heat of formation of boron oxide.

EXPERIMENTAL

The boron chloride in our possession was contaminated with chlorine, as was evident from its green color. It was purified with the aid of metallic mercury at 0°. The purity of the product so obtained was shown by the results of analysis of the solutions obtained in the calorimetric experiments; the mean molar ratio of HCl to H_3BO_3 in the solutions was 3.005, which corresponds with a purity of 99.87% for the BCl_3.

The heat of hydrolysis was measured in a calorimeter with an insulating envelope [10]. The envelope was kept at a temperature of 25° $\pm$ 0.01°. Hydrolysis was conducted in a glass calorimeter beaker of about 400 ml capacity. The experiments were performed as follows: the glass tube 5 (volume about 80 ml) is filled with BCl_3 vapor, and the tube is fitted into the circuit shown in Fig. 1. In the initial stage, air enters from a gasometer at 1, and is dried in the wash-bottles 2 and 3, containing sulfuric acid and phosphorus pentoxide, respectively, before going through the by-pass tube (tap 4 open, taps 6 and 7 shut) and the spiral 8, where it assumes the

temperature of the thermostatic envelope of the calorimeter, and then through the injector 9 into the calorimeter water 11.
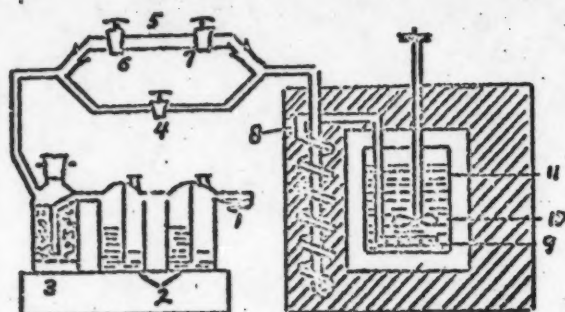

Fig.1. Diagram of apparatus: 1) entry of air from gasometer; 2) wash-bottles with sulfuric acid; 3) drying bottle containing phosphorus pentoxide on glass-wool; 4) tap of side-tube; 5) tube filled with boron chloride; 6 and 7) taps; 8) spiral; immersed in the thermostatic envelope of the calorimeter (diagonal shading); 9) a tube sealed at the end, with small openings for passage of gas; 10) a propeller stirrer; 11) calorimeter vessel containing water.

After completion of the initial stage of the experiment, tap 4 is closed, and taps 6 and 7 are opened, when the boron chloride in 5 is swept out into the calorimeter by a stream of dry air, entering the solution in the form of small bubbles, full absorption of which is facilitated by the action of the stirrer 10. The same amount (357 g) of bi-distilled water is taken in all cases. The final concentration of the solution amounted to about 6600 mol of water per mol of BCl_3.

The rise in temperature was measured by means of a Beckmann thermometer, calibrated by the All-Union Institute of Standards to an accuracy of $0.001°$; readings were taken every 30 sec. The main period of the reaction lasted about 2-3 min. The rise in temperature amounted to $0.5-0.6°$, and the rate of rise of temperature in the initial and final periods was $0.005-0.006°$ per min. Calorimeter corrections (for radiation, heat of vaporization of water, heat evolved by the stirrer) were calculated by the Regnault-Pfaundler-Usov formula, and amounted to 2-3% of the observed temperature rise. The method of determining the water equivalent of the calorimeter was the same as that previously described [10].

The solutions obtained were analyzed volumetrically, HCl by titration with NaOH, with methyl orange indicator, followed by titration of H_3BO_3 with phenolphthalein indicator after addition of mannitol [11]. Since the titrations of HCl were the more accurate, the number of moles of hydrolyzed BCl_3 was taken as being equal to one third of the number of moles of HCl formed. The accuracy of the final results for the heat of hydrolysis of BCl_3 is about 1.5%. The results obtained are given in Table 1.

TABLE 1

Results of experiments for determination of heat of hydrolysis of BCl_3
Water equivalent of calorimeter = 0.410 kcal per degree

Expt. No.	Temp. rise in °C (corrected)	No. of Millimoles			$\dfrac{HCl}{H_3BO_3}$	Heat of hydrolysis in kcal per mole
		HCl	H_3BO_3	BCl_3		
1	0.521	8.007	2.723	2.669	2.94	80.0
2	0.594	8.895	2.965	2.965	3.00	82.1
3	0.634	9.696	3.221	3.232	3.01	80.4
4	0.561	8.535	2.789	2.845	3.06	80.8
					Mean	80.8

The heat of formation of BCl_3 can be derived from the heat of hydrolysis of gaseous BCl_3 so found:

$$BCl_{3(gas)} + 6603 H_2O_{(liquid)} = H_3BO_{3\,(6600)} + 3HCl_{(2200)} + 80.8 \text{ kcal.}$$
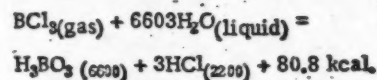
Knowing the heats of formation of liquid water and $HCl_{(2200)}$*, which are 68 37 and 39.61 kcal, respectively [12], we obtain for the heat of formation of of gaseous BCl_3.

$$Q^t_{BCl_3} = QH_{3BO_3} - 167.1 \text{ kcal.} \quad (1)$$

where $Q_{H_3BO_3}$ is the heat of formation of $H_3BO_{3(6600)}$.

According to Arisdalen and Andersen [7]

$$B_2O_{3(vitreous)} + 13203 H_2O_{(liquid)} = 2H_3BO_{3\,(6600)} + 7.96 \text{ kcal}$$
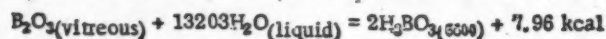
and hence

$$Q_{H_3BO_3} = \frac{1}{2} Q^t_{B_2O_3} + 106.5 \text{ kcal.} \quad (2)$$

* The figures in parentheses signify concentrations, expressed as moles of water per mole of dissolved substance.

where $Q_{B_2O_3}$ is the heat of formation of vitreous oxide.

We obtain from equations (1) and (2)

$$Q^o_{BCl_3} = \frac{1}{2} Q^o_{B_2O_3} - 60.6 \text{ kcal.} \tag{3}$$

The latent heats of vaporization and fusion of BCl_3 [12] [13], and the heat of transition of vitreous into crystalline B_2O_3 [6], are equal, respectively, to 5.68, 0.50, and 4.36 kcal per mol. It hence follows from equation (3) that :

$$Q_{BCl_3} = \frac{1}{2} Q_{B_2O_3} - 56.6 \text{ kcal,} \tag{4}$$

where Q_{BCl_3} is the heat of formation of crystalline BCl_3, and $Q_{B_2O_3}$ is the heat of formation of crystalline B_2O_3. Equation (4) relates the values of Q_{BCl_3} and $Q_{B_2O_3}$. In this way the determination of the correct value of the heat of formation of B_2O_3 is of importance for the determination of this constant for boron chloride.

Apart from Johnston, Hersch, and Kerr's [5] indirect derivation of $Q_{B_2O_3}$, there are three direct, and hence preferable, determinations of this value, as has been mentioned above [2], [3], and [4]. The first two of these are in close agreement, being 343.4 and 339.4 kcal (for crystalline B_2O_3); the mean value 341.4 kcal may be taken to represent both. The third value (285.5 kcal) is nearly 20% lower than the above mean value. Inasmuch as all three determinations appear to have been performed with equal accuracy it is not possible to decide which of the results to accept, without subjecting them to a theoretical analysis. We shall in the following section of this paper describe the way in which the selection of the correct values of heats of formation can be made.

THEORETICAL

According to the rule of thermochemical logarithmics, heats of formation, related to a single bond $\left(-\frac{\Delta H}{w}\right)$, are linear functions of the atomic number Z of elements. Within each group or period of the periodic table this holds for isoelectronic analogs [14] in the absence of "inversion points" (ρ), which may be established by crystallochemical data [15]. The application of the above-mentioned rule to the cross-checking of the basic thermochemical properties of compounds of Group III elements is of importance to the choice of the correct value of two possible values for the heat of formation of boron chloride. It would seem, however, that we here encounter very real difficulties, as appears from Table 2 and Fig. 2.
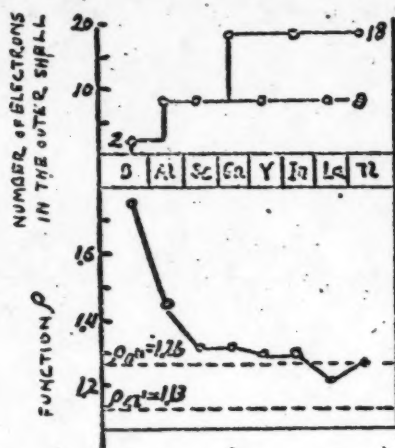

Fig. 2. Diagram of properties of ions of elements of Group III

TABLE 2

Properties of ions of Group III elements

Element	B	Al	Sc	Y	La	Ga	In	Tl
Atomic No. Z	5	13	21	39	57	31	49	81
No. of outer electrons of the cations	2	8	8	8	8	18	18	18
Function ρ	1.75	1.44	1.31	1.29	1.21	1.31	1.29	1.26

The cations of Group III elements fall into two "classes"; the ions possess an inert gas or an 18-electron shell, and in the former class the outer electron shell varies from 2 electrons for boron to 8 electrons for the others. In addition, the phenomenon of "inversion" should be observed in the case of the oxides.

It has been noted [14] that elements placed at the beginnings of groups deviate systematically from the rule of thermochemical logarithmics, and that the deviation is the greater the further is the group from the center one (Group IV). This interesting feature of the periodic system is fully explicable on the basis of modern conceptions of atomic structure. The atoms of the elements of any Group of the periodic system may be regarded as electronic analogs, in the case of the elements themselves, or of their covalent compounds. However, their ions are not complete electronic analogs, but only to the extent
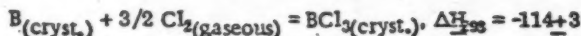
that they possess an identical architecture of their electron shell. Thus, or example, B, Al, Sc, Y, La, Ga, In, and Tl should, using Nekrasov's terminology [16], be regarded as being analogs, from the electronic standpoint (they all have 3 valency electrons), whereas in the form of ions only B, Al, Sc, Y, and La can be regarded as analogs, since they have an inert gas type of orbit, and are distinct from the 18-electron orbit ions Ga, In, and Tl, which are analogous to each other. But even the inert gas ions are not entirely uniform, since B gives a 2-electron cation, whereas the Al, Sc, Y, and La cations are 8-electron ones.

The further from the middle of the periodic system is the given group, and correspondingly the more clearly defined is the ionic nature of the bonds, the more distinctly will this difference in the structure of the inert gas ions appear. Thus, for example, in Group I the properties of lithium differ considerably from those of the other alkali metals, while in Group II the properties of beryllium differ much less from those of other elements of this group, being scarcely distinguishable in the case of the carbonates, and, finally, the elements of Group III show very uniform properties, boron scarcely differing from the other elements of this group in the general gradation of properties.
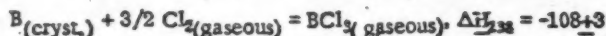
This explanation may also be based on quantitative data, using estimates of the "ionicity" of bonds, derived from electro-negativity measurements [17]. In the chlorides series this amounts to 60% for LiCl, to 40% for $BeCl_2$, and to 20% for BCl_3. It is to be expected that if the ionic type of bond dominates among the alkali chlorides, the difference between lithium and its analogs will depend on the differences between the electronic structures of the ions. For the first elements of Group III, however, it is resemblances between atom-analogs, rather than ion-analogs, which dominates, since the share of ionic forces is only 20%. Differences between inert gas type ions are no longer clear-cut; only the more definite differences between these ions and ions with an 18-electron orbit remain. For this reason boron should not give deviations from the rule of thermochemical logarithmics; this conclusion should at any rate be applicable to the chlorides, for which an "inversion point" does not exist: ρ_{Cl} is 1.13 less than the ρ of all the cations of Group III.

It might hence be concluded that the heat of formation of BCl_3, per g-equivalent within the given coordinates (Fig. 3), should lie on the same straight line as do the heats of formation of other chlorides of inert gas type ions of ele-

Fig. 3. Heat of formation of chlorides and oxides.

ments of Group III. We thus obtain a criterion for judging which of a number of values advanced is the correct one (satisfying the linear dependence of $-\Delta H/w$ on $\ln Z$). We see from Fig. 3 that $-\Delta H/w$ for BCl_3 as derived from the data of Eggersgluess, Monroe, and Parker [4] (crossed square) is inacceptable. The mean value ($-\Delta H/w = 31.4$) derived from Johnston, Hersch, and Kerr's results [5] is also doubtful, although it is not so far off the line. The value given by our measurements, on the other hand, considered together with the values of $\Delta H_{B_2O_3}$ obtained by Roth [1, 2] and by Todd and Miller [3], fully satisfies the criterion required above; the point lies on the curve.

We thus arrive at the following final results for the thermal effect of the reaction (in kcal per mole):

$$B_{(cryst.)} + 3/2\ Cl_{2(gaseous)} = BCl_{3(cryst.)}, \Delta H_{298} = -114 \pm 3$$

or

$$B_{(cryst.)} + 3/2\ Cl_{2(gaseous)} = BCl_{3\ gaseous}, \Delta H_{298} = -108 \pm 3$$

But, since the above value contains within it also the ΔH_{298} for B_2O_3 (cf. equation 4), we arrive at the conclusion that the results of Roth, and of Todd and Miller must be correct. They are practically identical, so that taking the mean (56.7 ± 0.2 kcal per g-equiv.), we obtain the following as the most reliable value:

$$2B_{(cryst.)} + 3/2\ O_{2(gas)} = B_2O_{3(cryst.)}, \Delta H_{298} = -341 \pm 3\ kcal/mole$$

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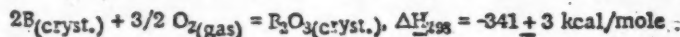
* The "ionicity" of the bond rises with increase in the atomic number of elements within each group.

or

$$2B_{(cryst)} + 3/2\ O_{2(gas)} = B_2O_{3(vitreous)}. \quad \Delta \underline{H}_{298} = -337 \pm 3\ \text{kcal/mole}.$$
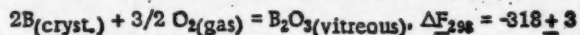
It follows from Fig. 2 that the inversion point for oxides of Group III elements appears only at the end of the group, and this cannot lead to the appearance of an inflexion in the $-\Delta H/w$ ln $\underline{Z}$ curve. The rule of thermochemical logarithmics should hence be followed here over the whole range. This is confirmed by Fig. 3 (II), which thus affords yet another proof of the correctness of our conclusions.

Although the part of Johnston, Hersch, and Kerr's work dealing with the heat of formation of B_2O_3 cannot, as we have shown, be considered to be acceptable, their entropy determinations must be considered to be wholly acceptable, without any reservations. Combining these results with those presented in the present paper we arrive at the following values for standard free energy, in kcal per mole.
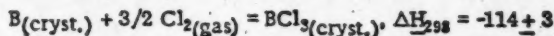
$$2B_{(cryst.)} + 3/2\ O_{2(gas)} = B_2O_{3(cryst.)}. \quad \Delta \underline{F}_{298} = -322 \pm 3$$

or

$$2B_{(cryst.)} + 3/2\ O_{2(gas)} = B_2O_{3(vitreous)}. \quad \Delta \underline{F}_{298} = -318 \pm 3$$
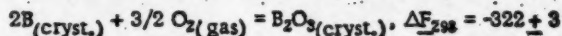
We wish to express our gratitude to L. C. Morozov for a supply of boron chloride, and to I. I. Lipilina for helping in the experimental work.
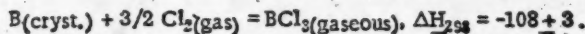
SUMMARY

1. The heat of hydrolysis of gaseous boron chloride has been determined.

2. Applying the concepts of electronegativity, of degree of ionicity of bonds, and of the function (see our previous communication) it has been shown that inversion cannot take place in the heats of formation of the series of chlorides B, Al, Sc, Y, and La, but that the rule of thermochemical logarithmics should be observed here. This allows of the derivation of the following values for heat of formation of BCl_3 (kcal per mole):

or

$$B_{(cryst.)} + 3/2\ Cl_{2(gas)} = BCl_{3(cryst.)}. \quad \Delta \underline{H}_{298} = -114 \pm 3$$

$$B_{(cryst.)} + 3/2\ Cl_{2(gas)} = BCl_{3(gaseous)}. \quad \Delta \underline{H}_{298} = -108 \pm 3.$$

3. The experimental values found for the heat of hydrolysis of BCl_3 show that the correct value for its heat of formation is in accordance with the expression

$$2B_{(cryst.)} + 3/2\ O_{2(gas)} = B_2O_{3(cryst.)}. \quad \Delta \underline{H}_{298} = -341 \pm 3.$$
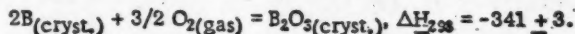
This confirms the work of Roth and Todd and Miller, but not of Eggersgluess, Monroe, and Parker, and also shows that the results calculated indirectly by Johnston, Hersch, and Kerr for the heat of formation of B_2O_3 are wrong.

4. Combining the measurements of specific heat (entropy) given by these authors with the results presented in the present paper, the following figure can be derived for the free energy of formation of boron oxide (kcal per mole:

$$2B_{(cryst.)} + 3/2\ O_{2(gas)} = B_2O_{3(cryst.)}. \quad \Delta \underline{F}_{298} = -322 \pm 3$$
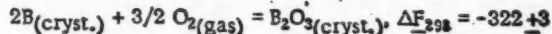
5. The rule of thermochemical logarithmics is followed without exception by the chlorides and oxides of the elements of Group III of the periodic system.

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MICRO-HARDNESS METHOD OF STUDYING INTRACRYSTALLINE LIQUATION

D. A. Petrov and L. A. Raikovskaya

1. NATURE OF THE PHENOMENON OF INTRACRYSTALLINE LIQUATION

Intradendritic or intracrystalline liquation of alloys is the term applied to non-uniformity of crystals of solid solutions of metals due to irregular distribution of their constituent parts during solidification. This non-uniformity is connected with disturbances of equilibrium taking place during crystallization as a result of retardation of diffusion processes due to excessive velocity of solidification.

The theoretical aspects of this problem have been discussed in detail by one of us [1], and we shall here repeat only the basic propositions. The crystallization of solid solution from the melt is shown by the phase diagram in the following way. As a liquid of composition c cools it becomes saturated with respect to crystals of solid solution at temperature t_1 (Fig. 1), and crystallization begins with further fall in temperature. The composition of the crystals separating initially is represented by the point $c_s^{\prime}$ on the phase diagram. As cooling proceeds, the composition of both phases changes continuously, of the liquid phase along the liquidus curve, and of the solid solution along the solidus curve. The alloy finally solidifies at t_4, with formation of a homogeneous solid solution, the composition of which from now corresponds with that of the alloy.

Since the composition of the solid solution does not remain constant, but changes continuously as crystallization proceeds, the conversion of the liquid into solid solution should be regarded as two parallel processes:
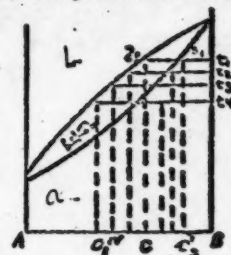
a) Actual formation of crystals of solid solution at temperature t (Fig. 2):

$$L_t \longrightarrow \alpha_t$$

b) Change in composition of crystals formed at higher temperature $t + dt$ (Fig. 2):

$$L_t + \alpha_{t + dt} \longrightarrow \alpha_t$$

Fig. 1. Scheme of crystallization of solid solution under equilibrium conditions.

Fig. 2.

The former process assumes diffusion only in the liquid phase, and it proceeds readily in molten metals. The latter process assumes diffusion to take place also in the solid phase, and this process is a slow one, becoming increasingly more difficult the lower the temperature. Diffusion in the solid phase may be completely abolished at high speeds of cooling, and at even higher speeds the same may apply to the liquid phase as well. We shall not here consider this case, but shall assume that diffusion proceeds without hindrance in the liquid phase. In the absence of diffusion in the solid phase the solid solution forming will not be a uniform one, but will represent an unbroken series of compositions, beginning with composition $c_s^{\prime}$ on Fig. 1.

The question arises, what will be the final term of this series of compositions? In other words, at what temperature will solidification of the melt be completed, in this case? . In the absence of diffusion in the solid phase the second of the above processes associated with conversion of liquid into solid solution, i.e., the change in composition of the solid solution

$$L_t + \alpha_{t+dt} \longrightarrow \alpha_t$$
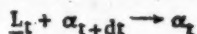
does not take place at all. As a result, all the liquid which would under equilibrium conditions have entered into

this process remains unsolidified at temperature t_4, which corresponds with completed crystallization of the alloy according to the phase diagram (Fig. 3).

In considering the process of crystallization of this part of the solution, beginning with temperature t_4, we similarly arrive at the conclusion that at temperature t_5 there will still remain unsolidified a certain part of the metal which was liquid at t_4, and at temperature t_6 some of the residual liquid from t_5 will still remain unsolidified, and so on. It follows that solidification of the melt will be completed only at the melting point of component A.

Reverting to the question of the non-uniformity of crystals of solid solution, we hence see that the degree of intra-dendritic liquation at high speeds of cooling is determined by the concentration interval between the composition of the initially forming crystals and the pure component with the lower m.p. It can, furthermore, be readily shown that in systems forming eutectic mixtures of solidification solutions of all alloys, in absence of diffusion in the solid phase, is completed at the eutectic temperature. The eutectic will, under these conditions, appear when even the least amount of the second component is added. In that case, the degree of intra-dendritic liquation, at high speeds of cooling, will be determined by the concentration interval between the composition of the initially formed crystals and of the crystals of solid solution saturated at the eutectic temperature.
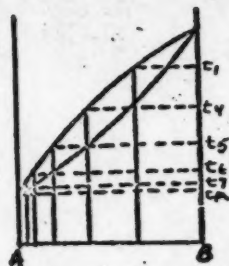

Fig. 3. Scheme of crystallization of solid solution under non-equilibrium conditions.

2. EXPERIMENTAL

Intracrystalline liquation was studied for alloys of aluminum with magnesium, and of bismuth with antimony. One of the methods used was that of measurement of micro-hardness, recommended for the study of non-uniformity of crystals by Bochvar and Zhadaeva [2].

Micro-hardness was measured by means of a diamond micro-indentor, which gives indentations of the order of $10\,\mu^2$ cross-section. With a grain size of the order of $10^3\,\mu^2$ (on polished surfaces) this indentor permits of hardness measurements at different parts of a single crystal. If the crystal is not homogeneous, owing to intra-crystalline liquation, variations in hardness are to be expected at different parts of the cross-section of the crystal. The formation of such a crystal may be considered as resulting from deposition of successive layers on the original crystal nucleus, so that the composition of the grain changes continuously from the center to the periphery.

If a solid solution of composition c (Fig. 4) crystallizes, the composition of the central part of the grain formed may correspond with c', while that of the peripheral zones of the grain will be c_1, i.e., that of the saturated solution of the solid solution at the eutectic temperature. If the line abd represents changes in the hardness of equilibrium alloys, then the hardness at the center of the grain will correspond to H_1, and at the periphery to H_2 (Fig. 4). For an alloy of a different composition, such as, for example c_1, the composition at the center of the grain will be c_1', and the hardness H_1', and the composition at the periphery will be c'', and the hardness H_2, as for the previous alloy. It is evident that with change in the content of the component B in the alloy, the composition of the center of the grain will change gradually, in the direction $A \rightarrow B$, approaching c^n, whereas the composition of the peripheral zones of the grains will remain the same for all alloys.

At the same time the hardness of the center of the grain will rise with increasing content of B in the alloy, according to a curve such as Curve 1, Fig. 4, whereas the hardness of the peripheral zones will lie on a horizontal line (Curve 2, Fig. 4). The curves approach each other as the content of B increases, until they intersect at a point corresponding with the composition of the eutectic alloy. In other words, differences in the composition, and hence in the hardness, of the center and the marginal zones of the grains, are the most marked in the case of alloys with a low content of B, and then gradually diminish until they vanish altogether in the case of eutectic alloys. The grains of solid solution separating from the eutectic alloy are of a uniform composition, irrespective of the rate of cooling. All values of hardness found at all parts of cross-section of grains are included between the two curves.

Alloys of antimony with bismuth (0 − 90% of Bi, at intervals of 10%) and of aluminum with magnesium (0, 1, 4, 8, 12 and 16% of Mg). The Sb-Bi alloys were cooled in an oven, and the Al-Mg alloys at room temperature, i.e., they were cooled comparatively slowly, so as to obtain fairly large grains. For air-cooled alloys the crystallization interval was 5-10 min., as compared to 20-30 min. for oven-cooled alloys. The largest grains present in the alloys were taken for hardness measurements, in order to obtain as full a picture as possible of distribution of hardness within single crystals.

The results of the measurements are shown in the diagrams Figs. 5 and 6. The length of the diagonals of the indentations in microns is given in the upper parts of the diagrams. The number of dots recorded against each composition represents the number of indentations made. The points on the same horizontal line all have the same size of indentation. Curves are drawn through the points corresponding with maximum and minimum values of diagonals of indentations. The lower parts of the diagrams give microhardness curves, derived from the values for the diagonals; the upper curves represent maximum values for hardness of solid solutions, taken from the results obtained for a number of grains of a given alloy, and the lower curve expresses minimum values obtained similarly. All intermediate values for hardness of grains lie between these two curves.

The diagram for Al-Mg alloys (Fig. 5) resembles the theoretical diagram, with the difference that the upper curve becomes rectilinear only above 4% of Mg. The difference between maximum and minimum hardnesses is greatest for alloys with 4% of Mg, being much smaller for alloys with 1% of Mg. This is evidently due to the circumstance that the degree of intra-crystalline liquation does not, at the rate of cooling applied to these alloys, attain a sufficiently high value to cause total suppression of diffusion in the solid solution. The lower curve rises smoothly, as was to be expected (cf. Fig 4). The eutectic point, at which the two curves of the system should intersect, is at about 34% of Mg, outside the limits of this diagram.

Fig. 4. Scheme of change of hardness within grains of solid solution under conditions of intra-crystalline liquation.

Fig. 7 (see plate p. 254-a) is a photomicrograph of a section of an alloy containing 8% of Mg. It is evident that the deepest indentations (minimum hardness) are toward the center of the grain, and the shallowest ones are at the periphery.

The hardness diagram for antimony-bismuth alloys is given by Fig. 6. These elements form a continuous series of solid solutions. In solidifying, the central part of a grain forms a solid solution, the composition of which varies continuously from alloy to alloy, from pure bismuth to pure antimony. The composition of the peripheral zones of the grains of all alloys will in the limiting case (with total suppression of diffusion in the solid phase during crystallization) be that of pure bismuth. For this reason, the upper curve of the hardness diagram (lower part of Fig. 6) for rapidly cooled alloys should resemble the hardness curve for a continuous series of solid solutions, i.e., it should be a curve with the convexity directed upwards, as was shown by Kurnakov. The lower curve of the hardness diagram should be in the limiting case a straight line, since it should for all alloys correspond with the hardness of pure bismuth.
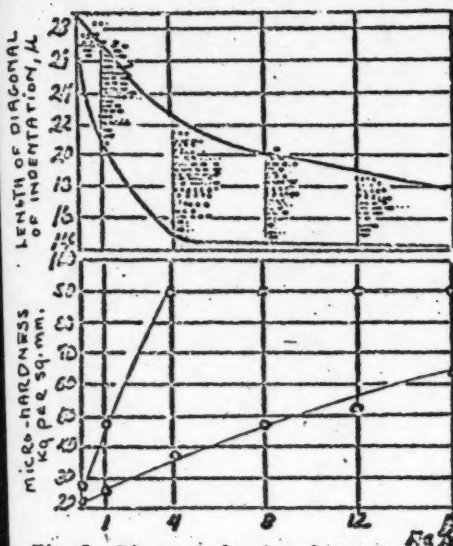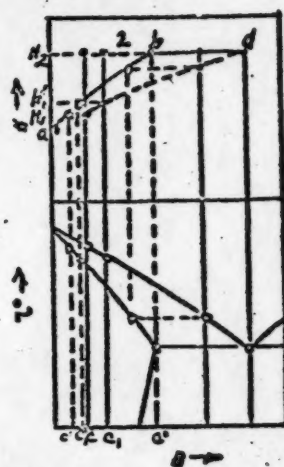

Fig. 5. Diagrams showing change in values of the diagonals of indentations and of micro-hardness in different zones of grains of solid solution Al-Mg.

The experimental curve is a straight line, gently sloping upwards to 50% of Sb, above which it rises more abruptly. As in the case of Al — Mg alloys, this is evidently due to the circumstance that at the given rate of cooling diffusion in the solid phase was not totally abolished. The photomicrograph of the 50% Sb alloy (Fig. 8) shows zones consisting preponderatingly of bismuth as black, and of antimony as light, areas; the deepest impressions (smallest hardnesses) are to be found in the black parts, and the most shallow ones in the light parts.

CONCLUSIONS

1. Intra-crystalline liquation of alloys of aluminum and magnesium and of bismuth and antimony has been

studied by the micro-hardness method.

2. The hardness of the alloys varies in accordance with the theoretical considerations previously advanced.

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[2] A. A. Bochvar and O.S. Zhadaeva, Bull. Acad. Sci. US.S.R., Div. Tech.Sci., 10-11 (1945).
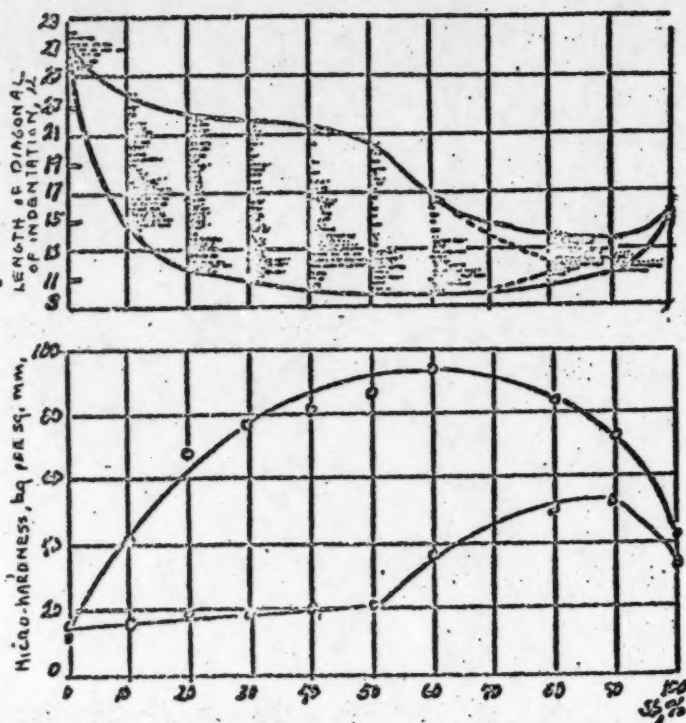
Fig. 6. Diagrams showing change in values of the diagonals of indentations and of micro-hardness in different zones of grains of solid solution Sb-Bi.

N.S.Kurnakov Institute of
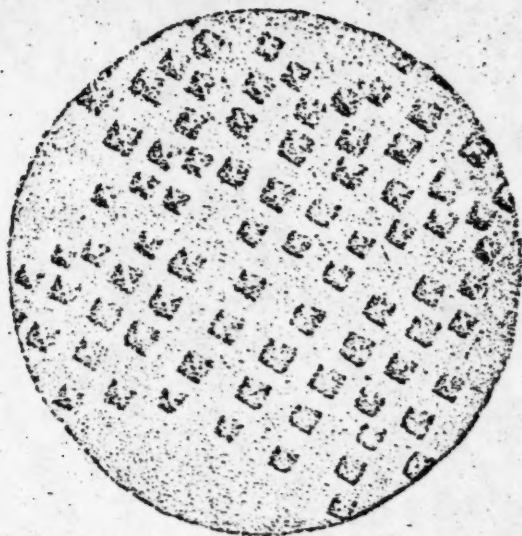General and Inorganic Chemistry,
Academy of Sciences, USSR

Fig. 7. Photomicrograph of indentations made on ground cross-sections of an alloy of Al with 8% of Mg. Cooled in air. (X 300).
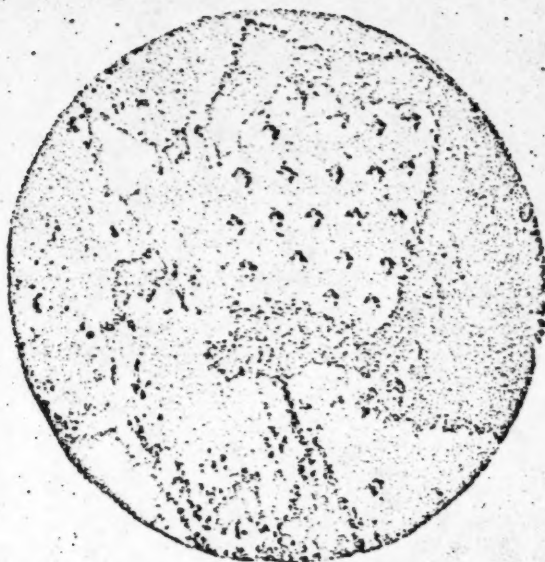

Fig. 8. Photomicrograph of indentations made on ground cross-sections of an alloy of Bi with 50% Sb. Cooled in an oven. Etched with 50% HNO$_3$. (X 300).

THERMODYNAMIC STUDY OF THE SYSTEMS CADMIUM - ZINC,

CADMIUM - LEAD, CADMIUM - TIN, BISMUTH - CADMIUM, TIN - ZINC, and LEAD - TIN

V. S. Lyashenko

The phase diagrams of binary metallic systems are at present in most cases sufficiently well known. We know that the formation of one or another phase is associated with energy changes, of the dimensions of which, and of the rules governing which, we in most cases know nothing.

The application of chemical thermodynamics, and in particular of the concept of thermodynamic activity, to the phase diagram enables us, as will be shown below, to calculate the free energy and the heat of formation of any particular phase separating from the molten alloy. We shall in this paper present a method for the calculation of the activity of components of binary systems in the liquid state, and we illustrate its application to the calculation of the free energy and the heat of formation of α- and β- phases in phase diagrams of the type corresponding with limited solubility in the solid state.

GENERAL PRINCIPLES

If a pure component separates along the liquidus line of a phase diagram then the free energy of its separation (solidification) and its activity, relative to the component in the liquid state, taken as the standard state, are given by the following expression [1]:

$$\Delta F = -RT \ln a_s \qquad (1)$$

Since the pure component separating out is in equilibrium with the same component in the liquid state, the activity a_s of the solid component will be equal to its activity in the liquid phase, a_1, at the temperature and composition given by the liquidus curve. If the solid phase separating out towards the side of component $\underline{A}$ of the phase diagram (Fig. 1) is the solid solution α, which may for low solubilities be taken as an ideal solution, then the activity of component $\underline{A}$ in the liquid phase, $\underline{a}_{A1}$, at the temperature and composition determined by the liquidus curve, will be

$$a_{A1} = a_{As} N_{A\alpha}. \qquad (2)$$

At temperature $\underline{T}$ the liquid phase, with activities of components $\underline{a}_{A1}$ and $\underline{a}_{B1}$, will be in equilibrium with the solid solution α, of composition $\underline{N}_{A\alpha}$ and $\underline{N}_{B\alpha}$ g-mol. Hence, expressing the reaction of formation of one gram-atom of solid solution by $N_{A\alpha} \cdot A + N_{B\alpha} B = \alpha$ and taking the activity of the solid solution as being equal to unity, the free energy of formation of the solid solution α of the given composition from the liquid phase will be given by

$$\Delta F = -RT \ln \frac{1}{a_{A1}^{N_{A\alpha}} \cdot a_{B1}^{N_{B\alpha}}} \qquad (3)$$

Having derived the free energy of formation of α-phase at different temperatures and compositions, in accordance with the given phase diagram, and knowing the relation

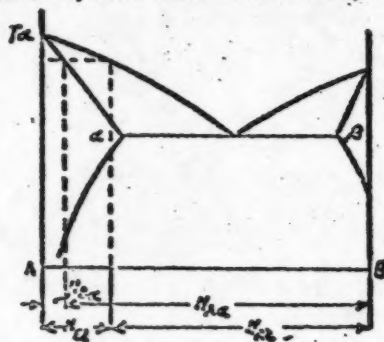$$\frac{d\Delta F/T}{d1/T} = \Delta H \qquad (4)$$

Fig. 1. Phase diagram for the case of limited solubility in the solid state.

derived from the Gibbs-Helmholtz equation, we construct a curve, with ordinates $\Delta F/T$ and abscissas $1/T$. The tangent of the angle between the tangent at the given point of the curve relating temperature with composition of the α-phase and the horizontal axis gives the value of the heat of formation of solid solution from the liquid phase.

It is necessary, in order to derive the heat of formation of solid solution from its solid components, to add to the heat of formation of solid solution from the liquid phase the heat of fusion of components A and B and to subtract or add the heat of mixing of the liquid components A and B, in proportions corresponding with those present in the α-phase. The heat of mixing should be added when the reaction of mixing the liquid components is endothermic, and subtracted when it is exothermic.

This method for calculating the activity of the components of liquid alloys, and of the free energy and heat of formation of solid solutions in systems with limited solid solubility, will be applied below to a number of systems. The system cadmium-zinc will be discussed most fully, only the experimental results and the curves being given for the other systems. We shall in this paper apply thermodynamic representation, i.e., if a process proceeds with evolution of heat, this will be designated by a minus sign. All calculations are related to a gram-atom of alloy.

THE SYSTEM CADMIUM-ZINC

Activity of cadmium and zinc in the system cadmium-zinc.

The phase diagram of the system cadmium-zinc has been exhaustively studied by a number of authors, and the relevant data, taken from Hansen's compilation [2] are given in Table 1. These data serve for supplying the necessary critical points for the thermodynamic treatment of the phase diagram.

TABLE 1

In Table 1 T is the temperature at which separation of α- or β-phase begins, at a molar concentration of cadmium in the liquid phase of N_{Cd_1}; N_{Cd_α} and N_{Zn_β} are the molar concentrations of cadmium and zinc, respectively, in the solid solutions α and β, in equilibrium with the liquid phases at the corresponding temperature.

N_{Cd_1}	0.9	0.8	0.734 eutectic	0.7	0.6	0.5	0.4	0.3	0.2	0.1
T_1	569	547	539	547	566	581	596	608	626	651
N_{Cd_α}	0.975	0.966	0.950	–	–	–	–	–	–	–
N_{Zn_β}	–	–	0.987	0.987	0.036	0.985	0.984	0.984	0.984	0.987

The specific heat of cadmium and zinc in the solid and liquid states, and their latent heats of fusion, are taken from the book "Thermal constants of inorganic substances" [3], and the equations relating latent heat of fusion to temperature are hence derived:

For cadmium $\quad \Delta H = 904 + 1.67 \cdot T - 1.233 \cdot 10^{-3} \cdot T^2$ $\qquad$ (5)

For zinc $\qquad \Delta H = 491 + 2.34 \cdot T - 1.075 \cdot 10^{-3} \cdot T^2$ $\qquad$ (6)

After substituting for ΔH in the Gibbs-Helmholtz equation, and integrating, we obtain the following expressions connecting free energy of fusion (solidification) with temperature:

For cadmium $\quad \Delta F = 904 - 1.67 \cdot T \ln T + 1.233 \cdot 10^{-3} \cdot T^2 + 8.415.$ $\qquad$ (7)

For zinc $\qquad \Delta F = 491 - 2.34 \cdot T \ln T + 1.075 \cdot 10^{-3} \cdot T^2 + 13.856.$ $\qquad$ (8)

where 8.415 and 13.856 are integration constants, following from the condition that at the melting point $\Delta F = 0$.

The activities of cadmium and zinc in the liquid phase are given in Table 2 (figures not in parentheses); the values are derived from equations (1), (7) and (8) for temperatures and compositions corresponding with those of the liquidus curve, up to, and including the eutectic point.

The calculation of the activities for any other temperature is performed by means of the equation

$$\frac{d \ln a}{dT} = -\frac{L}{RT^2}.$$

This equation is integrated between the limits T_1 to T_2, assuming $\overline{L}$ to be independent of temperature, and after substituting the values of constants we obtain:

$$\ln a_{T_2} = -\frac{\bar{L}}{4.575}\left(\frac{T_2 - T_1}{T_2 \cdot T_1}\right) + \ln a_{T_1} \qquad (9)$$

where $\bar{L}$ is the partial heat of mixing derived by a graphical method [1] from Kawakami's data for heats of mixing [4], and presented in Table 3.

Activities calculated by us for cadmium and zinc for temperatures of up to 700°K are presented in Table 4 (not those marked with an asterisk). The same Table also gives other data, the significance of which requires no explanation; these data will be required by us for the calculation of activities of cadmium and zinc

TABLE 2

N_{Cd_1}	0.9	0.8	0.734	0.7	0.6	0.5	0.4	0.3	0.2	0.1
T_1	569	547	539	547	566	581	596	608	626	651
a_{Cd}	0.919	0.865	0.838	(0.824)	(0.781)	(0.749)	(0.699)	(0.648)	(0.562)	(0.374)
a_{Zn}	(0.460)	(0.624)	0.717	0.732	0.769	0.792	0.816	0.840	0.867	0.919

not available to us. We know the activities of cadmium and zinc only up to the eutectic composition, from each side of the phase diagram, i.e., corresponding with the liquidus curves of the diagram.

TABLE 3

N_{Zn}	0.00	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$\bar{L}_{Zn}\ \dfrac{cal}{\text{g-atom}}$	1300	1232	1175	1025	925	500	246	185	138	46	0
$\bar{L}_{Cd}\ \dfrac{cal}{\text{g-atom}}$	0.0	0.0	16	64	117	486	762	875	1026	1156	2100

The remaining activities of zinc are calculated in the following way. A graph (Fig.2) is constructed, in which the ordinates are the ratio N_{Zn}/N_{Cd}, and the abscissas are $\log a_{Zn}/N_{Zn}$. The curve ends with the activity and the molar ratio for zinc at the eutectic composition; we continue it, along the broken line, to $N_{Cd}/N_{Zn} = 0$. From the Gibbs-Duhem equation

$$\int_0^{\log\frac{a_{Cd}}{N_{Cd}}} d\log\frac{a_{Cd}}{N_{Cd}} = \int_0^{\frac{N_{Zn}}{N_{Cd}}} \frac{N_{Zn}}{N_{Cd}} \cdot d\log\frac{a_{Zn}}{N_{Zn}}$$

by graphical integration, and with the known activities of cadmium at $N_{Cd} = 0.9$, 0.8, and 0.736, we obtain the following

$$\log\frac{a_{Cd}}{N_{Cd} = 0.8} = \log\frac{a_{Cd}}{N_{Cd} = 0.9} + \frac{bb^\circ + cc^\circ}{2}\ bc,$$

whence we derive $bc = \dfrac{(0.0323 - 0.0107) \cdot 2}{0.111 - 0.250} = 0.1203.$

And further,

$$\log\frac{a_{Cd}}{N_{Cd} = 0.734} = \log\frac{a_{Cd}}{N_{Cd} = 0.8} + \frac{aa^\circ + bb^\circ}{2}\ ab,$$

whence $ab = \dfrac{(0.0545 - 0.0323) \cdot 2}{0.250 + 0.365} = 0.0706.$

We see from Fig.2 that:

257

TABLE 4

N_{Zn}	$\dfrac{N_{Zn}}{N_{Cd}}$	a_{Zn}	$\dfrac{a_{Zn}}{N_{Zn}}$	$\log \dfrac{a_{Zn}}{N_{Zn}}$	a_{Cd}	$\dfrac{a_{Cd}}{N_{Cd}}$	$\log \dfrac{a_{Cd}}{N_{Cd}}$
0.9	9.00	0.916	1.018	0.0077	0.344*	3.436	0.5361
0.8	4.00	0.857	1.072	0.0302	0.515*	2.576	0.4114
0.7	2.33	0.823	1.177	0.0702	0.589*	1.965	0.2933
0.6	1.50	0.792	1.321	0.1206	0.635*	1.589	0.2011
0.5	1.00	0.736	1.473	0.1681	0.697*	1.394	0.1441
0.4	0.667	0.657	1.643	0.2156	0.766*	1.278	0.1061
0.3	0.428	0.590	1.968	0.2938	0.813*	1.163	0.0653
0.266	0.365	0.557	2.092	0.3212	0.832	1.134	0.0545
0.2	0.250	0.493*	2.466	0.3918	0.863	1.079	0.0328
0.1	0.111	0.325*	3.250	0.5121	0.922	1.025	0.0107

$$\log \frac{a_{Zn}}{N_{Zn}=0.2} = \log \frac{a_{Zn}}{N_{Zn}=0.266} + ab,$$

whence, after substitution of the appropriate
values, we obtain

$$\frac{a_{Zn}}{N_{Zn}=0.2} = 2.466; \quad a_{Zn} = 0.493.$$

Similarly,

$$\log \frac{a_{Zn}}{N_{Zn}=0.1} = \log \frac{a_{Zn}}{N_{Zn}=0.2} + bc,$$

whence

$$\frac{a_{Zn}}{N_{Zn}=0.1} = 3.25; \quad a_{Zn} = 0.325.$$

The missing activities of cadmium are found similarly, but in this case the ordinates of the curve are N_{Cd}/N_{Zn}, and the abscissas $\log a_{Cd}/N_{Cd}$. The activities of cadmium and zinc calculated in this way are marked with an asterisk in Table 4.

The relation between the activities of cadmium and zinc at 700°K and their relative molar concentrations is shown in Fig.3, which also shows activities for cadmium and zinc according to Taylor's data [5] for 708°K, derived from e.m.f. measurements, as well as Burmeister and Jellinek's results [6] for 955°K, derived from vapor pressure measurements. It is evident that our results are in good agreement with those of Taylor, but that Burmeister and Jellinek's results are in general lower than ours; this is ascribable to the higher temperature to which their results refer, since it is known that positive deviations of activity diminish with rising temperature.
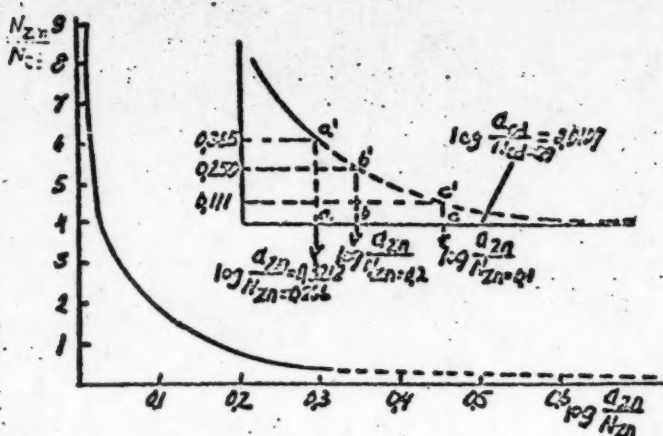

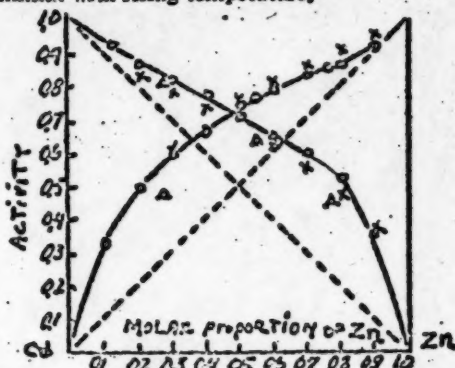Fig.2. Determination of missing activities of zinc in the system cadmium-zinc.

Fig. 3. Activities of cadmium and zinc in the system cadmium-zinc: o — our values, for 700°K; x — Taylor s values for 708°K; Δ — Jellinek's values, for 955°K.

Free energy and heat of formation of α- and β-phases in the system cadmium-zinc

The activities of zinc have first to be calculated before we can calculate the free energy of formation of the α-phase, from equation (3), at the temperature and composition corresponding to the liquidus curve for separation of α-phase, according to equation (9). We already have the corresponding values for cadmium, given in Table 2. Similar calculations are performed for derivation of the free energy of formation of the β-phase, in accordance with the temperature and composition determined by the liquidus curve for separation of β-phase. The results so calculated for the activity of zinc are given in Table 2 (in parentheses).

The calculated free energies, and the graphically derived heats of formation (Fig.4) of the α- and β-phases from liquid mixtures of the system cadmium-zinc, are given in Table 5, for various temperatures and compositions.

The curve relating $-\Delta E/T$ to $1/T$ is practically rectilinear for the α- and β-phases of the system cadmium-zinc, which suggests that the heat of formation of these phases from the liquid components is practically independent of temperature and composition, and amounts for the α-phase to -1580 cal per g-atom, and for the β-phase to -1430 cal per g-atom. This linear relationship between $-\Delta E/T$ and $1/T$ is not, as will appear below, found for solid solutions of variable composition separating from certain other systems.

From the values obtained for the heats of formation of the α- and β-phases from liquid mixtures, the latent heats of fusion of cadmium and zinc calculated from equations (5) and (7), and the heats of mixing of the liquid components, we derive the heat of formation of α-phase at the eutectic temperature from the solid components; the value found is -135 cal per g-atom (exothermic reaction), while for the β-phase it is 13 cal per g-atom, i.e., it is practically zero. Weibke and Kubaschewsky [7] found that the heat of formation of solid alloys

TABLE 5

α-phase					β-phase				
N_{Cd_1}	N_{Cd_α}	T_1	$-\Delta F \dfrac{cal}{g\text{-}atom}$	$-\Delta H \dfrac{cal}{g\text{-}atom}$	N_{Zn_1}	N_{Zn_β}	T_1	$-\Delta F \dfrac{cal}{g\text{-}atom}$	$-\Delta H \dfrac{cal}{g\text{-}atom}$
0.9	0.975	569	115	1580	0.9	0.987	651	126	1430
0.8	0.966	547	176	1580	0.8	0.984	626	186	1430
0.734	0.950	539	198	1580	0.7	0.984	608	217	1430
					0.6	0.984	596	244	1430
					0.5	0.985	581	270	1430
					0.4	0.986	566	295	1430
					0.3	0.987	547	337	1430
					0.266	0.987	539	354	1430

of this system from their solid components was practically equal to zero, as might be expected from the negligible mutual solubility of cadmium and zinc at 100° [2], while the formation of eutectic mixtures from their pure components should not be associated with any perceptible thermal effect. The free energy of formation of α-phase from the solid components, calculated similarly, amounts to -50 cal per g-atom, and of the β-phase to -14 cal per g-atom (neglecting, as being very small under the given conditions, change in free energy due to mixing).

Fig.4. Heats of formation of α- and β-phases from liquid alloys of the system cadmium-zinc

Cadmium-Lead, Cadmium-Tin, Lead-Tin, Bismuth-Cadmium, and Tin-Zinc Systems

Activities of cadmium and lead, cadmium and tin, lead and tin, bismuth and cadmium, and tin and zinc in the appropriate liquid systems.
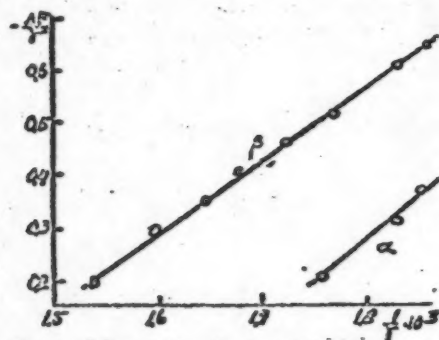
The critical points of the phase diagrams were taken from the data of a number of authors, as compiled by Hansen [2]. The solubility of lead in cadmium is taken as negligible. That of cadmium in lead at the eutectic temperature is taken from Tamman and Ruedger [2] as being equal to 0.0715 mol parts. The solubility of cadmium in tin and of tin in cadmium are taken from Le Blanc [2] as being 0.0787 and 0.0313 mol parts, respectively, at the eutectic temperature. The solubility of lead in tin and of tin in lead are taken from the figures of a number of authors quoted by Hansen [2] as being 0.015 and 0.297 mol parts, respectively, at the eutectic temperature. The mutual solubilities of the systems bismuth-cadmium and tin-zinc are taken as being negligible in the solid state.

The latent heat and the free energies of fusion of the components of the systems under consideration have been calculated for various temperatures from the thermal data given in the literature [3], using the following equations:

For lead $\Delta H = 970 + 1.03 \cdot T - 1.01 \cdot 10^{-3} \cdot T^2;$ (10)

        $\Delta F = 970 - 1.03 \cdot T \ln T + 1.01 \cdot 10^{-3} \cdot T^2 + 4.370 \cdot T.$ (11)

For tin $\Delta H = 1550 + 1.55 \cdot T - 2.40 \cdot 10^{-3} \cdot T^2;$ (12)

        $\Delta F = 1550 - 1.55 \cdot T \ln T + 2.40 \cdot 10^{-3} T^2 + 5.347 \cdot T.$ (13)

For bismuth $\Delta H = 1809 + 2.11 \cdot T - 1.22 \cdot 10^{-3} \cdot T^2;$ (14)

        $\Delta F = 1809 - 2.11 \cdot T \ln T + 1.22 \cdot 10^{-3} T^2 + 9.311 \cdot T.$ (15)

Equations (5), (7), (6), and (8) were used for cadmium and zinc. The partial heats of mixing, derived graphically from the heats of mixing [4] of the components of the systems, are given in Table 6.

TABLE 6

Mol. fraction of first component	System							
	Cadmium-lead, at 633°K		Cadmium-tin, at 623°K		Lead-tin, at 623°K		Tin-zinc, at 723°K	
	$\overline{L}_{Cd}$ cal g-atom	$\overline{L}_{Pb}$ cal g-atom	$\overline{L}_{Cd}$ cal g-atom	$\overline{L}_{Sn}$ cal g-atom	$\overline{L}_{Pb}$ cal g-atom	$\overline{L}_{Sn}$ cal g-atom	$\overline{L}_{Sn}$ cal g-atom	$\overline{L}_{Zn}$ cal g-atom
0.0	0.0	(2140)	0.0	(1300)	0.0	(1065)	0.0	(2800)
0.1	25	1867	15	1085	17	905	-38	2400
0.2	85	1537	45	915	44	768	115	1940
0.3	196	1212	86	790	73	668	222	1655
0.4	510	620	182	615	135	560	337	1445
0.5	702	373	318	455	434	198	1085	615
0.6	874	225	595	225	576	78	1495	237
0.7	1055	135	800	108	660	30	1750	110
0.8	1305	55	920	67	695	20	1955	35
0.9	1515	16	1215	20	742	12	2135	15
1.0	(1760)	0.0	(1600)	0.0	(810)	0.0	(2300)	0.0

According to Kawakami [4], the heat of mixing of liquid bismuth and cadmium at 350° is practically zero, for which reason the partial heat of mixing of these metals is also taken to be zero. The activities of cadmium and lead, cadmium and tin, lead and tin, bismuth and cadmium, and tin and zinc in the corresponding systems, calculated in the same way as for the system cadmium-zinc, are given in Table 7.

TABLE 7

Mol. fraction of first component	System									
	Cadmium-lead at 705°K		Cadmium-tin at 704°K		Lead-tin at 623°K		Bismuth-cadmium		Tin-zinc at 723°K	
	a_{Cd}	a_{Pb}	a_{Cd}	a_{Sn}	a_{Pb}	a_{Sn}	a_{Bi}	a_{Cd}	a_{Sn}	a_{Zn}
0.9	0.932	0.390	0.915	0.204	0.905	0.227	0.892	0.127	0.911	0.1975
0.8	0.898	0.498	0.844	0.321	0.836	0.363	0.798	0.241	0.819	0.368
0.7	0.870	0.551	0.798	0.405	0.781	0.455	0.702	0.357	0.731	0.519
0.6	0.807	0.636	0.718	0.492	0.715	0.536	0.616	0.455	0.651	0.642
0.5	0.765	0.681	0.641	0.564	0.626	0.633	0.524	0.554	0.549	0.792
0.4	0.712	0.725	0.549	0.647	0.543	0.712	0.428	0.654	0.493	0.862
0.3	0.654	0.761	0.442	0.736	0.453	0.786	0.329	0.751	0.459	0.894
0.2	0.514	0.822	0.318	0.820	0.360	0.848	0.252	0.820	0.407	0.928
0.1	0.287	0.907	0.182	0.900	0.239	0.907	0.141	0.904	0.345	0.949

Since the partial heat of mixing is, according to Kawakami [4] practically zero for bismuth and cadmium, the activities of bismuth and cadmium in the system bismuth-cadmium, given in Table 7, are not re-calculated for

any other temperature. The composition of the eutectic given by Hansen for this system is 40% by weight of cadmium, but the activities calculated on this basis do not give smooth curves for bismuth and cadmium. For this reason, we have taken the value of 39.1% by weight of cadmium as the composition of the eutectic, this figure being the mean of eight values derived by various authors.

Figs. 5, 6, 7, 8, and 9 give the curves relating calculated activities to mol concentration of the components of the systems. It is evident from Figs. 5, 6 and 9 that the calculated activities are in very good agreement with those obtained experimentally by Taylor [5] from e.m.f. measurements.

Jellinek's data [8] for the system tin-zinc at 973°K are somewhat below our calculated ones, as was to be expected, since positive deviations of activity from Raoult's law should diminish with rising temperature. Agreement is not so good, however, for the system bismuth-cadmium (Fig.8). We see that the calculated activities of cadmium exhibit positive deviations from Raoult's law over the whole range of concentrations; for bismuth positive deviations are found only in systems with a mol fraction of Bi of 0 to 0.6. Yet, according to Taylor's experimental results [5], alloys with a mol fraction of Cd of 0 to 0.6 should exhibit negative deviations, and the same applies to activities of bismuth in alloys containing 0 to 50 atomic-% of bismuth.

This difference between calculated and experimental values of activities cannot be ascribed to inaccurate determination of the liquidus curve, since this phase diagram has been subjected to adequate study by a number of authors [2]. Nor can it be due to inaccuracies in the published thermal data for bismuth and cadmium, since these are known to be sufficiently accurate [3], or to an error in the method adopted for the calculation, since our method is thermodynamically sound, and its validity is confirmed by the curves for a number of systems, given above.

Bearing in mind that, for the system bismuth-cadmium, the liquidus curve is situated somewhat above that which would follow from the theoretical position based on Schroeder's equation [9], it might be said that the system does not follow Raoult's law, since attractive forces between like atoms prevail over those between unlike atoms. The mixing of the liquid components should hence be associated with absorption of heat.

The negative deviations of activity of bismuth and cadmium shown by Taylor's results would indicate that attractive forces between unlike atoms should prevail, that mixing of the liquid components should be associated with a slight evolution of heat, and that the liquidus curves should lie below those calculated from Schroeder's equation; this is not in fact the case. We may therefore assume that the activities of bismuth and cadmium calculated by us for this sytem are closer to the real values.
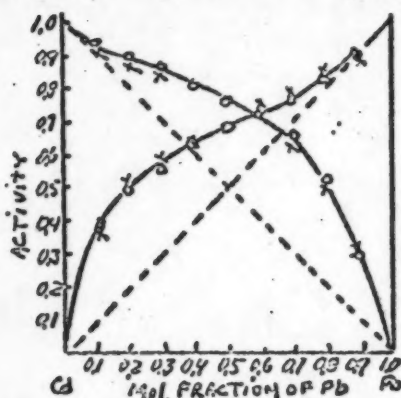
The calculated activities of lead and tin in the system lead-tin cannot be compared with experimental values, since it is not possible to determine these values by any known method, owing to the small differences between the electrode potentials and the vapor pressure of tin and lead. Thus our thermodynamic method of calculating the activities of the components of such systems is the only possible one.

Fig. 5. Activities of cadmium and lead in the system cadmium-lead: o - our values, for 705°K, x - Taylor's values, for 705° K.

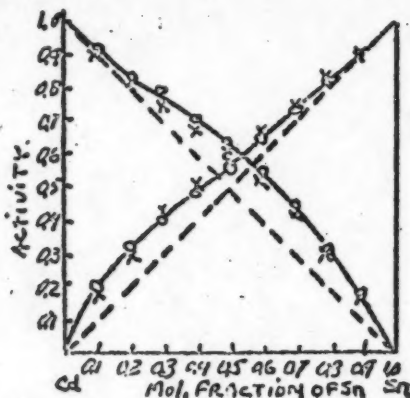Fig. 6. Activities of cadmium and tin in the system cadmium-tin: o - our values, for 704°K, x - Taylor's values, for 704°K.

Free Energy and Heat of Formation of Solid Solutions in the Systems Cadmium-Lead, Cadmium-Tin, and Lead-Tin

The free energy ΔF and the heat of formation ΔH of solid solutions from liquid mixtures in the given systems,
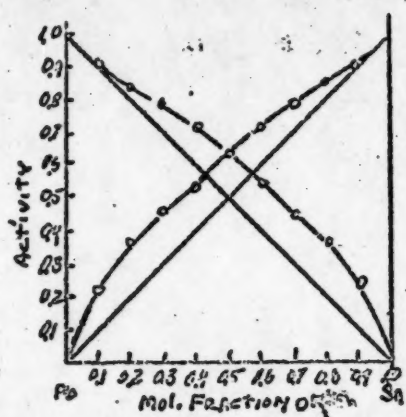
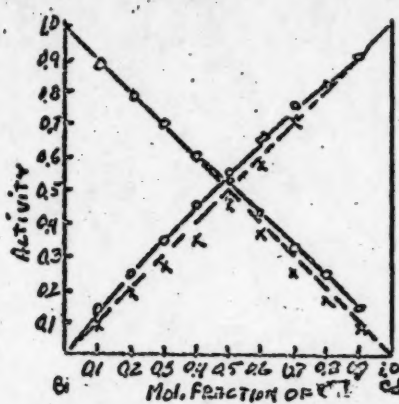Fig. 7. Activities of lead and tin in the system lead-tin: o - our values, for 623°K

Fig. 8. Activities of bismuth and cadmium in the system bismuth-cadmium: o - our results, x - Taylor's results, for 704°K.
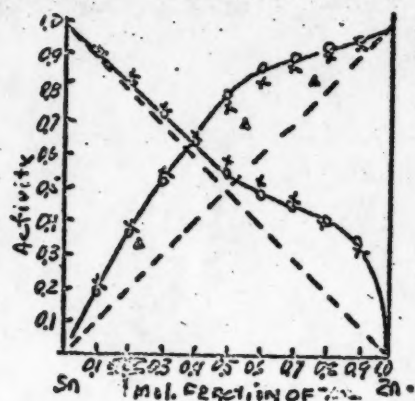

Fig. 9. Activities of tin and zinc in the system tin-zinc: o - our results, for 723°K x - Taylor's results, for 704°K, ▲ - Jellinek's results for 973°K.

and the heat of formation of solid solutions from the solid components, ΔQ, at the eutectic temperature, were calculated in the same way as for the system cadmium-zinc. The calculations were made only for the β-phase of the system cadmium-lead, since we take the solubility of lead in cadmium as being negligible. The results of these calculations are given in Table 8 and in Fig. 10, for the system cadmium-tin in Table 9 and Fig. 11, and for the system lead-tin in Table 10 and Fig. 12.

As may be seen from Figs. 10 and 11, the heat of formation of the β-phase of the systems cadmium-lead and cadmium-tin is practically independent of temperature and composition, while for the α-phase of the

TABLE 8

N_{Pb_1}	N_{Pb_β}	T_1	$-\Delta F$ cal per g-atom	$-\Delta H$ cal per g-atom	$-\Delta Q$ cal per g-atom
0.9	0.970	564	136	1464	295
0.8	0.946	535	205	1464	295
0.719	0.929	521	237	1464	295

system cadmium-tin the heat of formation is to a small extent dependent on temperature and composition, this dependence vanishing at the eutectic temperature. The heat of formation of α- and β-phases
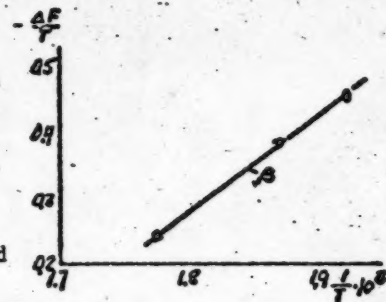

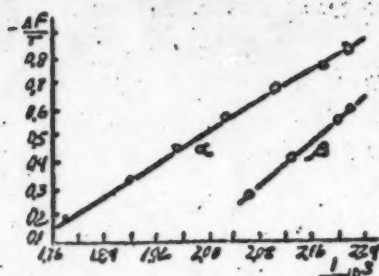Fig. 10. Heat of formation of β-phase from the liquid alloys of the system cadmium-zinc.

from liquid mixtures of the system lead-tin (Fig. 12) shows a high degree of dependence on temperature and composition; the ΔH of the α-phase falls, and of the β-phase rises, with diminution in temperature (Table 10).

The values calculated by us for the heats of formation of solid solutions from the solid components for the systems cadmium-lead and cadmium-tin cannot be compared with experimentally obtained data, since the only available published figures [Magnus and Mannheimer, 10] refer to alloys containing 50 atomic-% of each component, and not to the separate phases. Our figures for the system lead-tin are in agreement with published experimental data. Thus, Magnus and Mannheimer [10] came to the conclusion, on the basis of Taylor's and of their own experimental data, that formation of the α-phase should involve absorption of 400 cal. per g-atom, and of the β-phase evolution of 500 cal. per g-atom.

Fig. 11. Heat of formation of α- and β-phases from the liquid alloys of the system cadmium-tin.

Fig. 12. Heat of formation of α- and β-phases from liquid alloys of the system lead-tin.

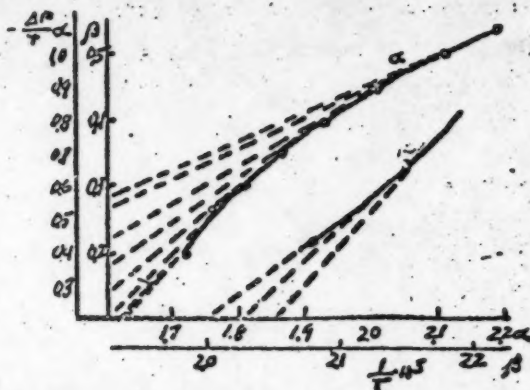## TABLE 9

	α-phase						β-phase				
N_{Cd_1}	N_{Cd_a}	T_1	−ΔF cal per g-atom	−ΔH cal per g-atom	−ΔQ cal per g-atom	N_{Sn_1}	N_{Sn_β}	T_1	−ΔF cal per g-atom	−ΔH cal per g-atom	−ΔQ cal per g-atom
0.9	0.993	561	105	1770	−	0.9	0.970	485	131	2100	−
0.8	0.987	533	179	1505	−	0.8	0.950	470	193	2100	−
0.7	0.982	513	233	1464	−	0.7	0.923	455	253	2100	−
0.6	0.978	493	276	1392	−	0.665	0.921	450	269	2100	294
0.5	0.974	475	319	1390	−						
0.4	0.971	459	338	1390	−						
0.261	0.969	450	377	1390	−47						

TABLE 10

	α-phase						β-phase				
N_{Pb_1}	N_{Pb_a}	T_1	−ΔF cal per g-atom	−ΔH cal per g-atom	−ΔQ cal per g-atom	N_{Sn_1}	N_{Sn_β}	T_1	−ΔF cal per g-atom	−ΔH cal per g-atom	−ΔQ cal per g-atom
0.9	0.942	584	204	2940	−	0.9	0.990	481	104	1350	−
0.8	0.902	574	285	2360	−	0.8	0.987	465	153	1770	−
0.7	0.863	552	334	1830	−	0.739	0.985	456	187	2100	392
0.6	0.824	536	381	1540	−						
0.5	0.793	517	412	1310	−						
0.4	0.758	497	446	1150	−						
0.3	0.719	470	476	910	−						
0.261	0.702	456	488	890	−694						

SUMMARY

1. A thermodynamic method is presented, for calculating activities of components of binary systems in the liquid state, which give eutectics on solidification. Activities calculated for the components of the systems cadmium-zinc, cadmium-tin, cadmium-lead, and tin-zinc are in full agreement with published values.

2. Activities have been calculated for lead and tin in the system lead-tin, for which these values have not yet been determined experimentally.

3. A thermodynamic method is given, for calculation of the heat and free energy of formation of solid

solutions in systems with a phase diagram of the limited mutual solubility type.

4. The heats of formation of the a- and β-phases of the system cadmium-zinc and of the β-phase of the system cadmium-lead from the liquid mixtures are practically independent of the temperature and composition.

5. The heats of formation of the a-phase of the system cadmium-tin, and of the a- and β-phases of the system lead-tin, from the liquid phases, vary according to temperature and composition of the phases separating out.

6. The heats of formation from their solid components of the a- and β-phases of the systems cadmium-zinc, cadmium-tin, and lead-tin, and of the β-phase of the system cadmium-lead, are -135, 13, 47, -294, 694, -392, and -295 cal. per g-atom, respectively.

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KINETICS OF POLYMERIZATION OF COMPOUNDS WITH CONJUGATED DOUBLE BONDS.

POLYMERIZATION OF METHYL ACRYLATE IN ABSENCE OF LIGHT

P. S. Shantarovich

We have shown in our previous communications [1, 2] that, in the polymerization of compounds with conjugated double bonds, the slow reaction, not activated by light, undergoes transition into a rapidly self-accelerating reaction when a certain critical depth of transformation, X_{cr}, characteristic of each compound, is achieved.

A detailed study of this stage of development of the reaction of polymerization has shown that the phenomenon of self-acceleration of the reaction occurs only when the insoluble form of polymer is produced. The formation and development of this high-molecular insoluble form of polymer, with its new properties, are signalled by the abrupt transition of the reaction into a self-accelerative one.

It was thought to be of interest to elucidate the connection between the observed increase in velocity beyond the critical point X_{cr} and the yield of insoluble form of polymer. Fig. 1, Curve 1* shows the kinetics of the reaction of polymerization of methyl acrylate in the absence of light, beyond the point X_{cr}. The variously designated points of Curve 1 show the closeness of coincidence of four curves obtained with different periods, t_e, of exposure to light [2]. The rectilinear curve 2 shows how the velocity of polymerization increases with increasing amount of polymer. The results of a study of the composition of the polymers obtained under these same conditions (different t_e) are given in Table 1, and are shown graphically in Fig. 2, in which the abscissas are total yield of polymer $X = X_a + X_\mu$, and the ordinates are yield of soluble polymer, X_a, or of insoluble polymer, X_μ, expressed as moles of transformed monomer. It appears from Table 1 and Fig. 2, that the insoluble form of polymer is practically absent until over 30% of the monomer has been transformed. It appears when the degree of polymerization attains the critical point X_{cr}, after which the yield of insoluble polymer rises rapidly, and may at any time be expressed by a value directly proportional to the general degree of polymerization. A similar relationship was found for the composition of the products of peroxide-promoted polymerization of chloroprene.
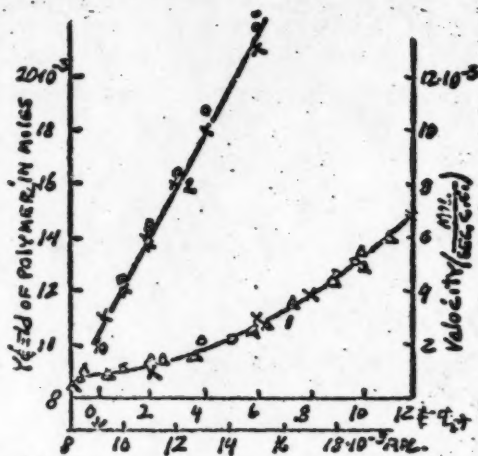

Fig. 1. Polymerization of methyl acrylate in absence of light. 1. Yield of polymer beyond the point X_{cr}; 2. Dependence of reaction velocity on X_μ (x - points obtained experimentally, o - points calculated from the equation): $x - t_e = 10$ min.; $o - t_e = 15$ min.; $\Delta - t_e = 24$ min.; $A - t_e = 32.5$ min. 1. Yield of polymer, in moles. 2. Velocity (mol./sec. c.c.)

DISCUSSION OF RESULTS

The equation

$$\frac{dn}{dt} = fn - k_0 X^{\frac{1}{2}} n^3 .$$

---

* $t - t_{cr}$ is the time counting from the moment of transition of the reaction, at point X_{cr}, into a self-accelerative one.

TABLE 1
Relation Between Soluble (α) and Insoluble (μ) Forms of Polymer

Left panel:

t_m time in hours	$\%$	$\cdot 10^{-3}$ mol.	α-form $\%$	$\cdot 10^{-3}$ mol.	μ-form $\%$	$\cdot 10^{-3}$ mol.

$t_e = 19$ min, $X_0 = 7.5\%$

t_m	$\%$	$\cdot 10^{-3}$ mol.	α $\%$	$\cdot 10^{-3}$ mol.	μ $\%$	$\cdot 10^{-3}$ mol.
5	10.5	2.97	10.5	2.97	—	—
30	16.75	4.6	16.75	4.6	—	—
85	33.0	9.07	16.75	7.07	—	—
87	33.66	9.25	16.75	7.0	10.2	2.8
89	35.46	9.85	—	7.3	—	—
91	40.0	11.0	—	7.1	13.7	3.8
95	48.3	13.2	—	—	20.0	5.5
97	54.49	15.1	—	6.9	28.3	7.8
98	58.2	16.3	—	7.2	34.6	9.5

$t_e = 24$ min, $X_0 = 18\%$

t_m	$\%$	$\cdot 10^{-3}$ mol.	α $\%$	$\cdot 10^{-3}$ mol.	μ $\%$	$\cdot 10^{-3}$ mol.
1	20.0	5.5	20.0	5.5	—	—
4	21.1	5.8	21.1	5.9	—	—
25	28.3	7.8	—	7.0	—	—
35	32.3	8.8	—	7.0	7.3	2.0
40	38.6	10.6	—	7.6	13.7	3.8
42	41.8	11.5	—	7.1	14.0	4.2
44	45.1	12.4	—	7.0	20.0	5.4
46	50.5	13.9	—	7.3	25.6	7.0
50	65.7	—	—	7.0	—	7.8

Right panel — Yield of polymers $X = X_\alpha + X_\mu$:

$t_e = 19$ min, $X_0 = 14\%$

t_m	$\%$	$\cdot 10^{-3}$ mol.	α $\%$	$\cdot 10^{-3}$ mol.	μ $\%$	$\cdot 10^{-3}$ mol.
1	15.7	4.32	15.1	4.32	—	—
4	17.2	4.7	17.2	4.1	—	—
10	18.7	5.2	18.7	5.2	—	—
30	24.5	6.7	—	6.0	—	—
50	32.1	8.8	—	6.4	7.3	2.0
54	36.7	10.1	—	6.5	14.6	4.0
56	40.4	11.1	—	7.0	14.2	4.4
60	49.1	13.5	—	7.8	16.7	4.6
62	58.0	16.0	—	7.1	32.7	9.0

$t_e = 33$ min, $X_0 = 24.5\%$

t_m	$\%$	$\cdot 10^{-3}$ mol.	α $\%$	$\cdot 10^{-3}$ mol.	μ $\%$	$\cdot 10^{-3}$ mol.
1	26.25	7.2	26.3	7.2	—	—
3	29.0	7.8	—	7.0	—	—
7	30.0	8.3	—	7.3	—	—
16	33.5	9.2	—	7.0	6.5	1.8
20	36.7	10.1	—	7.0	12.0	3.3
22	40.7	11.1	—	7.2	13.7	3.7
24	43.3	11.9	—	6.8	14.2	4.4
27	52.0	14.3	—	6.7	22.6	6.2

applies to the kinetics of the slow reaction of polymerization, proceeding in the dark, but does not apply to the period of rapid increase in velocity. The transition of the reaction at the point X_{cr} to one of rapid self-acceleration (Fig. 1) is obviously a manifestation of special conditions of development of the reaction in the three-dimensional structure of the polymer. With a "rigid" three-dimensional structure, the recombination factor may be made vanishingly small, and in that case the change with time in the number of active centers N in the polymer lattice is given by the equation
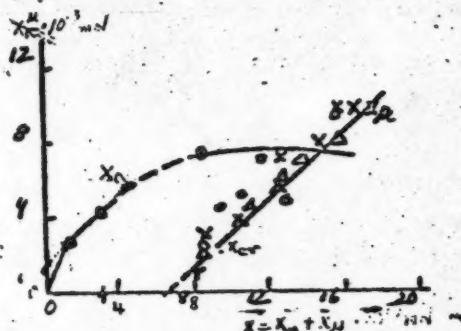
$$\frac{dN}{dt} = fN \tag{1}$$

and the velocity of polymerization, being a function of the amount of insoluble polymer forming, is given by the formula

$$\nu_\mu = \nu_{cr} + f X_\mu, \tag{2}$$

where ν_{cr} is the velocity of polymerization at the point X_{cr}, f is the branching factor, derivable from the slope of Curve 2 (Fig. 1) as the magnitude of the acceleration of the process in the polymer lattice, $X_\mu = X - X_{\mu cr}$. $X_{\mu cr}$ is the amount of insoluble polymer of methyl acrylate formed at the point X_{cr}.

Equation (2) for the velocity of the reaction in the lattice is valid only in the case when

$$\frac{N}{X_\mu} = \text{const.} \tag{3}$$

Dividing the equation (1) by $dX_\mu / dt = k_4 N$ we obtain

$$\frac{dN}{dX_\mu} = \frac{f}{k_4}, \tag{4}$$

where k_4 is the specific velocity of growth of the chain, and X_μ is the amount of polymer formed by polymerization within the lattice. This amount is expressed (according to the data of Table 1 and Fig. 2) by the linear relationship;

* t_m is time elapsed after extinguishing light.

Fig. 2. Relation between soluble (α) and insoluble (μ) forms of polymer, expressed as ratios of overall transformation. x - t_e = 10 min; o - t_e = 19 min; Δ - t_e = 24 min.

$$X_\mu = \alpha X_\mu - X_\alpha.\tag{5}$$

and hence

$$\frac{dN}{dX_\mu} = \alpha \frac{f}{k_4}.$$

Integrating within the limits X_{μ_0} (at the point X_{cr}) to X_μ, and from N_0 (number of active centers in the insoluble polymer formed at the point X_{cr}) to N_μ, we obtain

$$N = \alpha \frac{f}{k_4} X_\mu + [N_0 - \alpha \frac{f}{k_4} X_{\mu_0}].$$

It follows from this expression that the experimental dependence of the velocity on X_μ is possible only on the condition that

$$N_0 - \alpha \frac{f}{k_4} X_{\mu_0} = 0;$$

i.e., that

$$\frac{N}{X_\mu} = \frac{N_0}{X_{\mu_0}} = \alpha \frac{f}{k_4}\tag{6}$$

i.e., that the number of active centers in the lattice should grow in proportion to the mass of insoluble polymer.

Since the velocity of polymerization $dX_\mu/dt = k \cdot N$, we obtain from equations (5) and (6)

$$\frac{dX}{dt} = f X_\mu$$

and after integration within the limits X_{μ_0} to X_μ and from t_0 to t we obtain

$$X_\mu = X_{\mu_0} e^{f(t-t_0)}.\tag{7}$$

where t_0 is the moment of transition of the reaction to the self-accelerating type, and X_{μ_0} is the amount of insoluble polymer present at this moment. The accuracy of the conclusions arrived at may be checked [formulas (2) and (7)] with the aid of the mean values for velocity and yield of polymer derived from Curves 1 and 2 of Fig. 1, and from the straight line μ of Fig. 2; X_μ in formula 2 is understood to be

$$X_\mu = X_{\mu_{current}} - X_{\mu_{cr}}$$

The results of the check are given in Table 2.

TABLE 2

Calculation of Yield of Polymer and of its Rate of Production, Compared with Experimental Values

Time t_μ in hours	$X = X_\alpha + X_\mu$	X_μ		v_μ	
		Experimental values	Calculated from equation (7)	Experimental values	Calculated from equation (2)
	$\cdot 10^{-2}$	$\cdot 10^{-3}$	$\cdot 10^{-3}$	$\cdot 10^{-6}$	$\cdot 10^{-6}$
0.0	8.9	2.4	2.4	0.018	0.018
2.0	9.2	2.8	2.8	0.030	0.028
4.0	10.0	3.5	3.4	0.040	0.044
6.0	10.9	4.2	4.2	0.060	0.068
8.0	12.0	5.0	4.9	0.079	0.083
10.0	13.1	6.0	5.9	0.100	0.107
12.0	15.0	7.6	7.2	0.130	0.143

$t = 20°$; $X_{cr} = 2.4 \cdot 10^{-3}$ mole; $r_{cr} = 0.018 \cdot 20^{-6}$; $f = 2.5 \cdot 10^{-5}$

Good agreement is found between experimental and calculated values of the yield of polymer and of the velocity of polymerization, derived from formulas based on the experimentally justified assumption of the vanishingly small role of recombination of chains in the μ-polymer lattice. Equation (6) applies not only to methyl

acrylate, but also to the process of photo-polymerization of chloroprene, methyl methacrylate, and divinyl, and to the peroxide-promoted process of polymerization of chloroprene [3].

The insoluble polymers of methyl acrylate are, similarly to the μ- and ω- polymers of chloroprene, able to catalyze the polymerization of other compounds with conjugated double bonds. The active form of the polymers is obtained only when polymerization is conducted in the absence of a solvent, addition of even quite small amounts of which leads to production of only slightly active, or even of totally inactive, polymers. The condition that $c_m = 1$ is obligatory for production of active insoluble polymers. Dilution ($c_{in} < 1$) leads to degeneration of the branching process, which is replaced by simple vinyl polymerization with production of linear polymers.

CONCLUSIONS

1. The velocity of polymerization beyond the point X_{cr} is directly proportional to the amount of insoluble polymer formed at any given moment.

2. The expression N/X_μ = constant is shown to hold for polymerization within the lattice of the polymer (three-dimensional structure).

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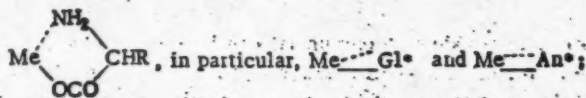# A NEW CLASS OF COORDINATION COMPOUNDS OF CHROMIUM WITH AMINO-ACIDS

L. M. Volshtein

It is known that α-amino-acids $NH_2CHR \cdot COOH$ can combine with atoms of complex-forming metals in various ways:

a) The metal may be bound to the radicals of the amino-acid forming a cycle, and occupying two co-ordination places

Me⟨NH₂ / OCO⟩CHR , in particular, Me---Gl• and Me---An•;

compounds in which such cycles are present are typical coordination complexes.

b) The metal (Me) may be bound to the amino-acid molecule in such a way as to occupy one co-ordination place: Me--- $NH_2CHR \cdot COOH$, in particular Me--GlH and Me—AnH.

c) The metal may be attached to an open amino-acid radical, occupying one coordination place: Me — $NH_2CHR \cdot COO$, in particular, Me—Gl and Me—An.

Up till now, the various forms of bonds between amino-acids and metals were realized in practice only for platinum compounds [1-9], such as [PtGl₂], [Pt(GlH)₄]Cl₂, Ba[PtGl₄], etc. For copper, cobalt, chromium, and palladium the only known compounds were those containing cyclically bound amino-acid radicals, i.e., the internally complex salts [CuGl₂], [CoGl₃], [CrGl₃], and [PdGl₂] (and the analogous alanine derivatives).

We have prepared about 30 new compounds of chromium with amino-acids (glycerine and alanine); they represent a peculiar and interesting class of co-ordination compound. We present in this paper a general review of these compounds, and give a short description of the results of a physico-chemical study of their aqueous solutions.•• Chugaev in 1910 [13] obtained compounds of chromium with glycine, of the composition CrGl₃ and CrGl₂OH, as well as the compound with alanine CrAn₃. Ley [1], repeating Chugaev's work in 1912, obtained another compound with alanine, to which he gave the formula CrAn₂OH + H₂O.

We have made a detailed study of these compounds, and have confirmed Chugaev's assumption (using electro-conductivity and other data) that the compounds [CrGl₃] and [CrAn₃] belong to the class of internally complex salts. It has been shown [10] that the compound of the composition CrGl₂OH is a bi-nuclear diol complex structure [Gl₂Cr⟨OH / OH⟩CrGl₂], and that the compound to which Ley assigned the formula CrAn₂OH + H₂O is in fact [11] not a hydroxo-aquo-compound, but is a bi-nuclear diol compound [An₂Cr⟨OH / OH⟩CrAn₂], analogous to the above glycine compound. These bi-nuclear compounds are broken down by prolonged boiling with hydrochloric acid, to give the compounds [CrGl₂H₂OCl] and [CrAn₂H₂OCl], which have been isolated by us.

All four compounds obtained by the above-named authors contain glycine or alanine in the form of cyclically linked radicals, each of which occupies two co-ordination places. Compounds in which chromium is co-ordinated with molecules of glycine (GlH) or alanine (AnH) were first described by us.

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* We introduce the following conventional symbols: radicals of glycine and alanine forming a cycle are represented by Gl and An; co-ordinated molecules of glycine and alanine, and also free glycine and alanine, are represented by GlH and AnH; open radicals of glycine and alanine, occupying only one co-ordinate place, are represented by Gl and An.
•• A few uncoordinated references relating to some of these compounds have been published earlier [10-12]. For a detailed exposition of the whole research see the author's thesis: "Coordination compounds of tervalent chromium with the simpler amino-acids" (Moscow, Institute of General and Inorganic Chemistry, Academy of Sciences (1950).

Certain French biochemists (Hugounenq, Florence) [14, 15] have suggested formulas for glycine derivatives of chromium, which they believe to contain glycine molecules coordinated to the chromium. We have shown how mistaken was these authors' treatment of the nature of these compounds; they did not even realize that the Gl radicals and the GlH molecules are absolutely different component parts of coordinate compounds. In fact, these authors were dealing with the same compounds which Chugaev had long before prepared.

All the above-mentioned authors conducted their studies of the reactions of tervalent chromium compounds with amino-acids exclusively in alkaline solution. Thus Chugaev, and after him Ley, added excess of glycine (or alanine) to solutions of tervalent chromium salts, which they heated, and then gradually added caustic alkali or ammonia. The reaction was of the following type:

$$CrCl_3 + 3GlH + 3NaOH \longrightarrow [CrGl_3] + 3NaCl + 3H_2O. \tag{1}$$
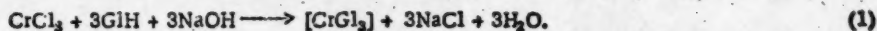
The reaction of salts of tervalent chromium with amino-acids in the absence of alkali, and with the solutions remaining acid throughout, has not yet been studied.

EXPERIMENTAL

Preparation of new compounds

We first established that heating solutions of tervalent chromium salts with excess of glycine (or alanine) leads to complex formation, without addition of alkali. The heated solutions change color, and do not give reactions for chromium ion. The final color of the solutions depends on the number of moles of glycine (or alanine) combining with each gram-atom of chromium (this number will hereafter be designated by n), and on the concentration of the initial solution. If the concentration of the initial chromium chloride solution was about 0.7M, the solutions obtained will have the following colors: $n = 3$, green, $n = 4$, violet, and $n = 5,6$, or more, red. Addition of caustic alkali or ammonia to the solutions obtained does not precipitate chromium hydroxide from them, either in the cold or after prolonged boiling, if $n \geqslant 3$. The solutions may be stored for a long time, and may be evaporated down to fairly small volume, without deposition of any sort of solid phase (at n values of 2 to 6; at $n > 6$ excess of glycine or alanine deposits).

As the solutions are evaporated down, they become more and more viscous, finally to yield vitreous, noncrystalline, intensely colored solid products, which are readily soluble in water. It is evident that the solutions obtained cannot contain the internally complex salts $[CrGl_3]$ and $[Cr_2Gl_4(OH)_2]$ (or $[CrAn_3]$ and $[Cr_2An_4(OH)_2]$, which are only very slightly soluble in water.

It is possible that earlier workers in this field had noticed that complex formation took place during heating of salts of chromium with glycine or alanine (although no mention of this is made in the literature), but that, since they could see no trace of any precipitates forming, they added alkali, and so shifted the reaction in the direction of formation of internally complex salts. We, however, were interested in the products formed in the solutions in absence of alkali. Our experiments showed that addition of excess of alcohol or acetone to the concentrated solutions (by evaporation down to small volume) leads to separation of a highly viscous product (an "oil"), above which is the colored supernatant aqueous-alcoholic or aqueous acetone solution. The "oil" solidifies after prolonged drying, yielding a non-crystalline product.

We added glycine to known volumes of chromium chloride solutions of known concentration, to give values of n of 2,3,4,5, and 6, and the solutions were boiled down to small volumes. Excess of acetone was then added, when the complex salt separated as an "oil", which was separated from the supernatant layer, washed with acetone, and dried to constant weight at 105-110°. Solid products were so obtained, of constant and reproducible composition, corresponding with the formulas: $CrCl_3$, H_2O, 2GlH; $CrCl_3$, 3GlH; $CrCl_3$, 4GlH; $CrCl_3$, 5GlH; $CrCl_3$, 6GlH.

The products obtained with $n = 1$ had variable compositions, which were not reproducible.

It may be supposed that the initial reaction taking place when solutions of chromium chloride are heated with glycine is

$$[Cr(H_2O)_6]Cl_3 + nGlH \rightleftharpoons [Cr(H_2O)_{6-n}(GlH)_n]Cl_3 + nH_2O. \tag{2}$$
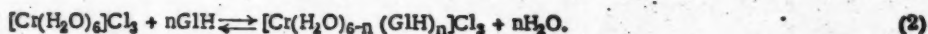
At the same time, Cl ions enter the inner sphere, leading to an equilibrium such as that illustrated below for the particular case $n = 3$:

$$[Cr(H_2O)_3(GlH)_3]Cl_3 \rightleftharpoons [Cr(GlH)_3Cl_3] + 3H_2O. \tag{3}$$
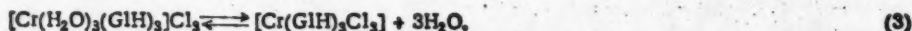
Concentration of the solutions by evaporation causes displacement of the equilibria (2) and (3) to the right, and the addition of acetone to the concentrated aqueous solutions causes precipitation of products of the compositions:

$[Cr(GlH)_2H_2OCl_3]$, $[Cr(GlH)_3Cl_3]$, $[Cr(GlH)_4Cl_2]Cl$, $[Cr(GlH)_6Cl]Cl_2$ and $[Cr(GlH)_6]Cl_3$.
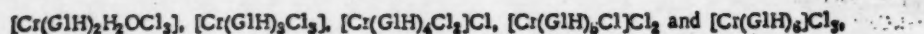
Further experiments confirmed the truth of these suppositions as to the nature of the compounds separating, with molecules of amino-acid coordinated with the chromium.

A second method of preparing compounds of this sort was based on the following reasoning. Before we had performed our experiments it might have been supposed that the reaction of GlH with $CrCl_3$ would proceed according to equation (4):

$$CrCl_3 + 3GlH \longrightarrow [CrGl_3] + 3HCl. \tag{4}$$
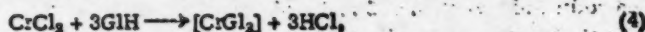
The reaction between GlH and chloroplatinite [3] does, in fact, proceed similarly:

$$K_2PtCl_4 + 2GlH \longrightarrow [PtGl_2] + 2HCl + 2KCl.$$
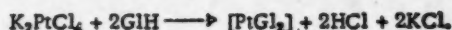
The fact that $[CrGl_3]$ is not obtained from $CrCl_3$ and GlH in absence of alkali led us to the conclusion that glycine cycles coordinated with chromium should be readily opened by hydrochloric acid. For this reason the reaction between GlH and $CrCl_3$ does not proceed according to equation (4), but according to equation (5), which is, for the particular case n = 3, the sum of equations (2) and (3):

$$CrCl_3 + 3GlH \longrightarrow [Cr(GlH)_3Cl_3]. \tag{5}$$
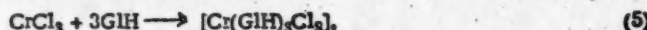
Experiments in fact showed that $[CrGl_3]$ readily goes into solution when boiled with 0.1M hydrochloric acid. If 3 or more moles of HCl are taken per mole of $[CrGl_3]$, and the solution is evaporated down to small volume, from which addition of acetone causes separation of a green syrup. This is dried to constant weight, to give a product of constant composition $CrGl_3$, 3HCl. The composition and properties of this product are identical with those of the substance obtained by addition of GlH to $CrCl_3$, for the case n = 3 (the identity of $CrGl_3$, 3HCl with $CrCl_3$, 3GlH is obvious). The opening of the glycine cycles corresponds with the equation:

$$[CrGl_3] + 3HCl \longrightarrow [Cr(GlH)_3Cl_3]. \tag{6}$$
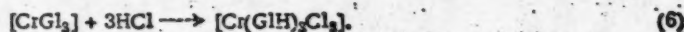
In this reaction the link between chromium and the carboxyl groups of the cycles is broken, and the radicals Gl become GlH molecules. The Cl anions then enter into the inner sphere, to occupy the places so vacated. This process may be represented schematically as follows:
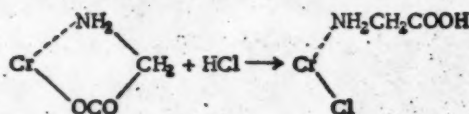

The action of acids (HCl, $H_2C_2O_4$) on the internally complex salts $[CrGl_3]$, $[CrAn_3]$, $[Cr_2Gl_4(OH)_2]$ and $[Cr_2An_4(OH)_2]$ provides us with a second method of preparing compounds in which GlH (AnH) molecules are coordinated with chromium, and we have prepared numerous compounds by this method. When 1 mole of HCl is taken per mole of $[CrGl_3]$ only one of the Gl cycles undergoes opening, and addition of acetone to the solution gives a compound of the composition $[CrGl_2(GlH)Cl]$. With 2 moles of HCl per mole of $[CrGl_3]$ 2 Gl cycles are opened, and the compound $[CrGl(GlH)_2Cl_2]$ is obtained. The following chlorides were obtained similarly from $[CrAn_3]$: $[CrAn_2(AnH)Cl]$, $[CrAn(AnH)_2Cl_2]$, and $[Cr(AnH)_3Cl_3]$.

Successive opening of Gl cycles, with introduction of C_2O_4 or C_2O_4H residues into the inner sphere, is similarly found when oxalic acid is taken instead of hydrochloric acid. With one mole of $H_2C_2O_4$ per mole of $[CrGl_3]$ the reaction proceeds according to the equation:

$$[CrGl_3] + H_2C_2O_4 \longrightarrow [CrGl(GlH)_2C_2O_4]. \tag{7}$$
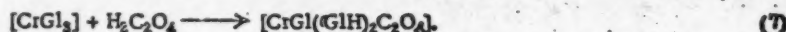
Solutions of the compounds $[CrGl(GlH)_2C_2O_4]$, $[Cr(GlH)_3C_2O_4(C_2O_4H)]$ and $[Cr(GlH)_3(C_2O_4H)_3]$ were thus obtained, and the compounds themselves were precipitated by adding excess of alcohol. By acting on $[CrGl_3]$ with hydrochloric and oxalic acids simultaneously the following compounds are obtained: $[Cr(GlH)_3ClC_2O_4]$, $[Cr(GlH)_3Cl(C_2O_4H)_2]$ and $[Cr(GlH)_3Cl_2(C_2O_4H)]$.

As mentioned above, fission of the complex occurs when one mole of the salt $[Cr_2Gl_4(OH)_2]$ or $[Cr_2An_4(OH)_2]$ is treated with 2 moles of HCl, according to the equation:

$$\left[Gl_2Cr \begin{matrix} OH \\ \\ OH \end{matrix} CrGl_2 \right] + 2HCl \longrightarrow 2[CrGl_2H_2OCl]. \qquad (8)$$
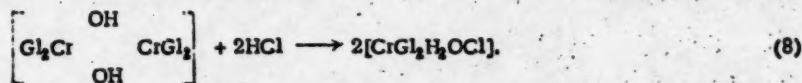
The product, or its alanine analog $[CrAn_2H_2OCl]$, is precipitated from the concentrated solutions by addition of acetone. The further action of HCl on these monochlorides leads to opening of the Gl cycles and to production of the trichlorides $[Cr(GlH)_2H_2OCl_3]$ or $[Cr(AnH)_2H_2OCl_3]$, and of the dichlorides $[CrGl(GlH)H_2OCl_2]$ and $[CrAn(AnH)H_2OCl_2]$.

Prolonged boiling of a solution of 2 moles of oxalic acid and 1 mole of $[Cr_2Gl_4(OH)_2]$ affords a product of the composition $[CrGl(GlH)H_2OC_2O_4]$ by the following reaction:

$$\left[Gl_2Cr \begin{matrix} OH \\ \\ OH \end{matrix} CrGl_2 \right] + 2H_2C_2O_4 \longrightarrow 2[CrGl(GlH)H_2OC_2O_4]. \qquad (9)$$
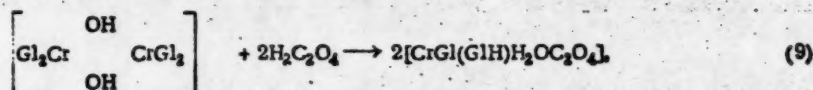
which involves fission of the bi-nuclear complex, with opening of two of the four glycine rings. At the same time part of the original binuclear salt undergoes hydrolysis, with production of chromium hydroxide. The precipitate of $Cr(OH)_3$ is filtered off, and the filtrate is evaporated down to a concentration of about 20% of the main product of the reaction $[CrGl(GlH)H_2OC_2O_4]$, which is then precipitated by addition of alcohol. A compound of the composition $[Cr(GlH)_2H_2OC_2O_4(C_2O_4H)]$ is also obtained by the action of oxalic acid on the bi-nuclear salt, and the compounds $[Cr(GlH)_2H_2OClC_2O_4]$ and $[Cr(GlH)_2H_2OCl(C_2O_4H)_2]$ are given by the action of HCl and $H_2C_2O_4$ together.

Some of the above compounds may be isolated from their aqueous solutions by evaporating these to dryness, on condition that strictly stoichiometric quantities of reagents are taken for their preparation. The vitreous masses obtained are dried to constant weight at 105-115°, to give products of constant and reproducible compositions.

A more general method for their preparation is to precipitate them from their concentrated aqueous solutions by addition of excess of alcohol or acetone. This leads to separation of extremely viscous "oils", which are the actual salts, still retaining small amounts of water. The colored "oils" become even more viscous when washed with alcohol or acetone, and, after separation from the aqueous alcoholic or the aqueous acetone layer, they are dried at 60-70° in order to eliminate organic solvent. The resulting vitreous mass is dried at 105-115°, ground to a powder in an agate mortar, and dried to constant weight. The variously colored powders so obtained in many cases have the outward appearance of crystalline substances, but X-ray and microscopic examination shows the absence of crystalline structure. Their composition was shown by analysis to be constant and reproducible.

It was found that the use of alcohol for separation of chlorine-containing complexes is not permissible, as they remove part of the hydrogen chloride, which remains in the alcoholic layer as ethoxonium chloride. Thus addition of alcohol to an aqueous solution of the compound $[CrAn_2(AnH)Cl]$ leads to the reaction

$$[CrAn_2(AnH)Cl] + C_2H_5OH \rightleftharpoons [CrAn_3] + [C_2H_5OH_2]Cl, \qquad (10)$$
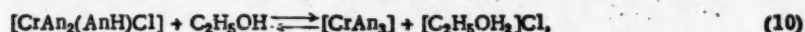
and the "oil" separating is contaminated with some $[CrAn_3]$, which is insoluble in alcohol.

Acetone is suitable for the separation of all compounds. Some of our compounds (such as $[CrGl(GlH)_2C_2O_4]$) are fairly soluble in glycol or glycerol, from which they may be reprecipitated by addition of excess of absolute alcohol; the product is a readily filtrable precipitate, and not the "oil" which would have been obtained from systems containing water. These precipitates are collected on a sintered glass filter, washed thoroughly with absolute alcohol, and dried to constant weight. Analysis of the precipitates shows that their structure is unaffected by this treatment.

General Review of Compounds

The group of compounds in which GlH or AnH molecules are coordinated with chromium may be considered as a special class of coordination compounds, having the following common properties: high solubility in water, high hygroscopicity, high viscosity of concentrated solutions, rising rapidly with rise in concentration, gradual transition from very viscous solutions to vitreous solids, insolubility in most organic solvents, property

of separating as an "oil" from concentrated aqueous solutions on addition of excess of alcohol or acetone, tendency towards formation of polymeric multi-nuclear complexes, absence of crystalline structure in the solid state, and possession of marked acidic properties. Two other compounds, $[CrGl_2H_2OCl]$ and $[CrAn_2H_2OCl]$, have similar properties to the compounds of this class, although GlH or AnH molecules do not enter into their composition. However, the action of water on some of the glycine (alanine) cycles in aqueous solutions, causing their opening, confers upon these compounds some of the properties of the above class, although to a modified degree only.

The compounds with glycine are subdivided into groups, from diglycyl to hexaglycyl derivatives; the numerals (di-, tri-, etc) refer to the number of GlH molecules of Gl radicals entering into the composition of a given compound.

Table 1 below presents 11 types of glycine compounds of which we have prepared representatives. In the formulas X represents an acidic residue; we have prepared compounds in which $X = Cl$, or C_2O_4H, or $\frac{1}{2}C_2O_4$. We were not able to prepare compounds of the monoglycyl series (the compound $[CrGl(H_2O)_2C_2O_4]$ was actually obtained, but could not be isolated in a sufficiently pure form).

The Table also includes the internally complex salts $[CrGl_3]$ and $\left[Gl_2Cr \begin{matrix} OH \\ \\ OH \end{matrix} CrGl_2 \right]$, which were taken as the starting point for preparation of all the other substances. All the types of compounds are genetically interconnected. The compounds from above down represent the products of the action of acids (opening of cycles), and from below up the products of the action of alkalis (closing of cycles); from left to right we have the products of replacement of H_2O or Cl by glycine.

TABLE 1

Series				
Diglycyl	Triglycyl	Tetraglycyl	Pentaglycyl	Hexaglycyl
$[Gl_2Cr \begin{matrix} OH \\ \\ OH \end{matrix} CrGl_2]$	$[CrGl_3]$			
$[CrGl_2H_2OX]$	$[CrGl_2(GlH)X]$	$[CrGl_2(GlH)_2]X$		
$[CrGl(GlH)H_2OX_2]$	$[CrGl(GlH)_2X_2]$	$[CrGl(GlH)_3X]X$		
$[Cr(GlH)_2H_2OX_3]$	$[Cr(GlH)_3X_3]$	$[Cr(GlH)_4X_2]X$	$[Cr(GlH)_5X]X_2$	$[Cr(GlH)_6]X_3$

Compounds of the di- and tri-glycyl series should formally be classed as non-electrolytes (tri-acido-triammine type), since all the component parts of the complex are included within the inner sphere, having zero charge. The initial internally complex salt $[CrGl_3]$ is a non-electrolyte, both in the formal sense and in reality; its molecular conductivity is very close to zero. The other compounds of the triacido-triammine type are converted into compounds of other types when dissolved in water, owing to their reactions with the solvent. The electrolytic dissociation of hydrated complexes (water is introduced into the inner sphere) is a result of this process.

Thus, for example, the chlorides of the triglycine series obtained from $[CrGl_3]$, viz., $[CrGl_2(GlH)Cl]$, $[CrGl(GlH)_2Cl_2]$, and $[Cr(GlH)_3Cl_3]$, are only in the formal sense non-electrolytes, since in aqueous solution replacement of inner sphere atoms of chlorine by water takes place, to give the corresponding 2-, 3-, and 4-ionic electrolytes $[CrGl_2(GlH)H_2O]Cl$, $[CrGl(GlH)_2(H_2O)_2]Cl_2$, and $[Cr(GlH)_3(H_2O)_3]Cl_3$. Moreover, owing to elimination of H ions from inner sphere GlH molecules the electro-conductivity of the solutions considerably exceeds that which would be expected from the structure of the hydrated complexes as given above.

Oxalates of the di- and tri-glycine series, such as $[CrGl(GlH)_2C_2O_4]$ and $[CrGl(GlH)H_2OC_2O_4]$, are much more nearly non-electrolytes, since the oxalic acid residues C_2O_4 are firmly held within the inner sphere. They too, however, owing to production of H ions from inner sphere GlH molecules, give solutions having a small (as compared with chlorides) electro-conductivity. Compounds such as $[Cr(GlH)_2(C_2O_4H)_2]$, which are formally non-electrolytes, in fact exhibit considerable electro-conductivity, since all of the inner sphere radicals (C_2O_4H and GlH) are able to produce H ions. Compounds of the tetra-, penta-, and hexa-glycyl series, such as $[Cr(GlH)_4Cl_2]Cl$, $[Cr(GlH)_5Cl]Cl_2$, and $[Cr(GlH)_6]Cl_3$, belong, respectively, to the diacido-tetrammine, the acido-pentammine, and the hexammine types, and are, with a tervalent central Cr atom, accordingly 2-, 3-, and 4-ionic electrolytes. Apart from this, they all form H ions from their inner spheres, so increasing the electro-conductivity of their solutions.

We see that a complex chain of reactions takes place in aqueous solutions of the substances under review.

273

We give below the more important of these transformations.

1. Replacement of inner sphere chlorine by molecules of water. As a result non-electrolytes become electrolytes, or the type of ionic dissociation changes

$$[\cdots Cr-Cl]^0 + H_2O \rightleftarrows [\cdots Cr---OH_2]^. + Cl^. . \tag{11}$$

2. Coordinated molecules of amino-acids (GlH or AnH) are displaced, and replaced by water:

$$[\cdots Cr---GlH] + H_2O \rightleftarrows [\cdots Cr---OH_2] + GlH. \tag{12}$$
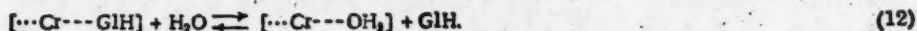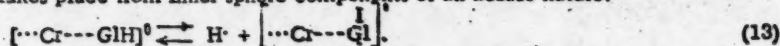
Direct evidence of the existence of such processes is given by the separation, after long standing, from solutions of the complexes

$$[CrGl(GlH)_2C_2O_4] \text{ and } [CrGl(GlH)H_2OC_2O_4]$$
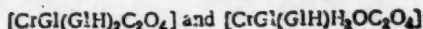
of the corresponding monoglycyl compound, of the composition $[CrGl(H_2O)_2C_2O_4]$.

3. Production of H ions takes place from inner sphere components of an acidic nature:

$$[\cdots Cr---GlH]^0 \rightleftarrows H^. + \left[\cdots Cr---\overset{I}{Gl}\right]. \tag{13}$$

Addition of alkali intensifies elimination of H ions, and the $\overset{I}{Gl}$ radicals so formed tend towards cycle closure, in some cases thereby giving internally complex salts.

4. Polymerization (association) takes place in concentrated solutions:
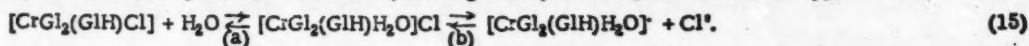
$$n[\cdots Cr---] \rightleftarrows [\cdots Cr_n---]. \tag{14}$$

The result is that solutions of any of the compounds contain a large number of derived complex and simple particles.

Study of the physico-chemical properties of aqueous solutions of the compounds

It was found necessary to study the electro-conductivity, the acidity (pH), and the viscosity of their solutions in order to elucidate the nature of the above compounds, as well as to carry out cryoscopic determinations of their molecular weights. It is evident that when compounds possess considerable acidic properties the mere measurement of the electro-conductivity of their solutions cannot serve as a basis for making assumptions regarding their type of ionic dissociation, and for determining their coordination formulas. It is essential that pH measurements should be made at the same time as conductivity determinations. Having determined the pH, and so knowing the corresponding hydrogen ion concentration [H$^.$], it is necessary, knowing the mobility of H ions, to calculate their contribution to the value for molecular conductivity, which we shall designate as μ_H. The value of μ_H so found is subtracted from that found for molecular conductivity (μ), since it is only the difference ($\mu - \mu_H$) which is characteristic of the type of ionic dissociation of our complexes, and which can serve for the determination of their co-ordination formulas. Not only are H ions produced in acidic dissociation, but the charges of the complex radicals from which the H ions are eliminated undergo change. The effect of this change in the charge of the complex particles is, however, insignificant in comparison with that of the appearance of H ions, since the mobility of the large complex ions is, as we shall see, 12-14 times smaller than is that of H ions (25-30 mho per ion-equivalent at 25°, as compared with a mobility for H ions of about 350 mho. For this reason, the contribution due to acidic dissociation can in most cases be derived from the value of the contribution due to hydrogen ions, μ_H.

The values for the differences ($\mu - \mu_H$) for solutions of compounds containing chlorine in the inner sphere rise with time to a maximum, at which they remain constant. This effect is a consequence of gradual replacement of inner sphere chlorine by molecules of water, leading finally to an equilibrium of the type:

$$[CrGl_2(GlH)Cl] + H_2O \underset{(a)}{\rightleftarrows} [CrGl_2(GlH)H_2O]Cl \underset{(b)}{\rightleftarrows} [CrGl_2(GlH)H_2O]^. + Cl^. . \tag{15}$$

In sufficiently dilute solutions (0.001M) the maximum values for $\mu - \mu_H$ correspond with complete transformation of the original complexes into the corresponding aquo-compounds. The maximum values for $\mu - \mu_H$ in 0.001M solutions of compounds containing 1 atom of chlorine in the inner sphere, such as, for example, $[CrGl_2(GlH)Cl]$ or $[CrGl_2(H_2O)Cl]$, amount to about 100 mho. Where there are two or three chlorine atoms within the inner sphere, such as in the compounds $[CrGl(GlH)_2Cl_2]$ or $[Cr(GlH)_3Cl_3]$, the maximum values of $\mu - \mu_H$ in 0.001M solutions are about 200 or 300 mho, respectively. The values of $\mu - \mu_H$ found correspond, respectively, with 2-, 3-, and 4-ionic electrolytes, such as, for example, $[CrGl_2(GlH)H_2O]Cl$, $[CrGl(GlH)_2(H_2O)_2]Cl_2$, and $[Cr(GlH)_3(H_2O)_3]Cl_3$, formed as a result of total replacement of chlorine from the inner sphere. Increase in the concentration of the solutions of compounds containing inner sphere chlorine leads to an abrupt fall in maximum values of $\mu - \mu_H$, which is due to diminution in the degree of hydration [a shift to the left of equilibrium (a) in equation (15)].

The values of $\mu - \mu_H$ found for chlorides such as $[CrGl_2(GlH)_2]Cl$ or $[Cr(GlH)_6]Cl_3$, which do not contain

any inner sphere chlorine, do not change with time, nor are they greatly affected by changes in concentration. The constant value of $\mu - \mu_H$ for 0.001M [CrGl$_2$(GlH)$_2$]Cl is 102 mho., which is the same as that of 0.001M solutions of chlorides with one chlorine atom in the inner sphere, such as [CrGl$_2$(GlH)Cl] and others.

The values of $\mu - \mu_H$ in solutions of compounds not containing any chlorine, i.e., in the case of oxalates, such as, for example, [CrGl(GlH)$_2$C$_2$O$_4$]or[Cr(GlH)$_5$C$_2$O$_4$C$_2$O$_2$H] are close to zero. This shows that the conductivity of such solutions is due exclusively to acidic dissociation of inner sphere radicals; if this cannot take place the compounds are practically non-electrolytes.

The results of a study of the electro-conductivity of their solutions (allowing for acidic dissociation) confirm the coordination formulas arrived at for the compounds on chemical grounds.

Measurements of the conductivity of solutions of the compound [CrGl$_2$(GlH)$_2$]Cl led to the determination of the mobility of the complex ion [CrGl$_2$(GlH)$_2$]', which was found to be about 27 mho. About the same value was found for the mobility of the other complex ions studied by us.

Measurements of the acidity (pH) of solutions of compounds belonging to one and the same series showed a regular increase in acidic properties as the number of glycine cycles opened rises. Thus, for example, the pH found for 0.001M solutions of [CrGl$_3$], [CrGl$_2$(GlH) Cl], [CrGl (GlH)$_2$Cl$_2$] and [Cr(GlH)$_3$Cl$_3$] were 7.06, 4.40, 3.97, and 3.56, respectively. It was found that, for compounds not containing Gl cycles, such as [Cr(GlH)$_3$Cl$_3$], the change in [H'] due to varying the concentration agrees satisfactorily with the dilution law.

We have already mentioned that the concentrated aqueous solutions of the compounds described by us have an exceptionally high viscosity. We have studied the rise in relative viscosity (η) of the solutions as their concentration is increased from low to very high values. It appears that the relative viscosity of dilute solutions is of the order usually found for corresponding concentrations. The value of η rises sharply as the concentration increases. These findings are illustrated by Table 2, which gives relative viscosities for solutions of the monochloride of the triglycyl series, [CrGl$_2$(GlH)Cl], at 25°.

TABLE 2

% in solution	6	31.0	18.6	53.3	58.0	63.8	66.1	70.0	73.7
η	1.14	2.31	10.0	15.3	28.0	127	237	560	5970

We determined the time of flow of the solutions applying different additional pressures, and found that Poiseuille's law is applicable to the solutions examined, which did not exhibit structural viscosity, characteristic of colloidal solutions. We investigated the relation between the composition of the compounds and the relative viscosity of their solutions at the same molar concentrations (7.62 molecules of water per molecule of dissolved substance, in all cases). The results are given in Table 3, for 11 compounds; η is relative to that of water, all at 25°.

We see in all three vertical columns that the value of η rises steeply with increase in the number of GlH molecules coordinated with chromium, i.e., with increase in the number of H$_2$O molecules or Cl atoms replaced by glycine. It is evident (horizontal rows) that increase in the number of molecules of GlH coordinated with chromium, and originating from opening of glycine cycles, is associated with increase in η as we pass from monochlorides (two Gl cycles) to dichlorides (one Gl cycle). Opening of the last Gl cycle, however, as seen in transition of dichlorides to trichlorides, leads to diminution of η (there is little further change in the tetraglycyl series).

The molecular weight of some of our compounds was determined by the cryoscopic method in aqueous solution. Since these compounds undergo electrolytic dissociation in aqueous solution it was necessary to determine not only the freezing point of the solutions, but also their pH and their conductivity, in order to allow for the contribution made by ions (Cl', H', and complex cations) towards the overall depression of freezing point.

We intend in a future paper to give a detailed description of the assumptions and methods used for the calculation, from the experimental data obtained for these complex cases, of the molecular weights of our coordination compounds. The complexity is due to the following: the non-electrolytes when in solution undergo conversion into electrolytes (e.g., [CrGl(GlH)H$_2$OCl$_2$] into [CrGl(GlH)(H$_2$O)$_3$]Cl$_2$), and at the same time production of H ions from coordinated GlH molecules, displacement of coordinated GlH molecules by water, and polymerization processes take place in the solutions.

TABLE 3

	Compound	
	η	
$[CrGl_2(H_2O)Cl]$ 171	$[CrGl(GlH)(H_2O)Cl_2]$ 350	$[Cr(GlH)_2(H_2O)Cl_3]$ 222
$[CrGl_2(GlH)Cl]$ 500	$[CrGl(GlH)_2Cl_2]$ 1157	$[Cr(GlH)_3Cl_3]$ 665
$[CrGl_2(GlH)_2]Cl$ 675	$[CrGl(GlH)_3Cl]Cl$ 1645	$[Cr(GlH)_4Cl_2]Cl$ 1728
		$[Cr(GlH)_5Cl]Cl_2$ 3833
		$[Cr(GlH)_6]Cl_3$ 6708

It was found that the values obtained for molecular weight in dilute solutions are close to those expected for monomeric molecules. The molecular weights rise gradually with increasing concentration of the solutions. Table 4 gives the values found for freshly prepared solutions of the monochloride $[CrGl_2H_2OCl]$.

The molecular weight of the monomeric form of $[CrGl_2H_2OCl]$ should be 253.6, which is in fact found for 0.02 and 0.05M solutions. The value found is very considerably higher than the theoretical for 0.1M solutions and for 0.5M solutions it is 2.2 times greater than would be expected for the monomer. The dichloride $[CrGl(GlH)H_2OCl_2]$ is more highly polymerized in solution, the apparent molecular weight in 0.2M solution being 2030, which is 7 times greater than that of the monomer (290.05).

It was found that the values found for the molecular weights of compounds in solutions prepared from the solid substances diminish with time after dissolution, to become, in the case of not very concentrated solutions, finally constant, and close to thewalues for the monomers. The more concentrated is the solution, the more slowly is this final value achieved, and the more does it exceed that of the monomer. This is illustrated by the values for the molecular weight of $[CrGl(GlH)H_2OCl_2]$ found in 0.2M solutions at different times after dissolution, as given in Table 5.

TABLE 4

Concentration	0.02 M	0.05 M	0.067 M	0.1 M	0.2 M	0.5 M
Mol. wt.	252	248	289	358	417	563

The final value of 316 for the molecular weight remains constant, within the limits of experimental accuracy. The final value for 0.5M solutions was 375, after very prolonged standing; the molecular weight of the monomer is 290. The molecular weight of this same compound in solutions prepared in two different ways was compared. One solution (0.2M) was prepared in the usual way, by dissolving a weighed amount of solid $[CrGl(GlH)H_2OCl_2]$. For the second solution, the compound was synthesized by the reaction $[Cr_2Gl_4(OH)_2] + 4HCl \longrightarrow 2[CrGl(GlH)H_2OCl_2]$, in dilute solution, which was then concentrated in a vacuum desiccator to the required concentration of 0.2M. In the former solution, the molecular weight was at first 7 times greater than that of the monomer, gradually falling to 316. In the latter solution, the molecular weight found was 288, which coincides with that of the monomer; it did not change with time, and differs little from the final value obtained for the first solution (316).

It is thus evident that polymeric molecules are present only in solutions prepared from solid substances, and that these polymeric molecules gradually depolymerize in dilute solutions. If, however, the dilute solutions are prepared from compounds synthesized in even more dilute solution, and not isolated in the solid state, normal values are found for the molecular weights. We would add that the changes in the experimentally found values of molecular weight of compounds in passing from one group of them to another are paralleled by the changes in viscosity of their solutions.

Possible mechanism of polymerization of the compounds

The extremely high viscosity of concentrated aqueous solutions of the compounds, the continuous transition from highly viscous liquids, which can be drawn out as long, thin threads, to vitreous, non-crystalline solid phases, and other observations, suggested to us the possibility of presence of polymeric (associated) complexes in the solutions of the compounds prepared by us. Direct determination of their molecular weight by the cryoscopic method confirmed this supposition, and showed that depolymerization (dissociation of associated complexes) takes place when the solutions are diluted.

We suppose that, in concentrated solutions, the molecules of complexes containing $NH_2CHR\cdot COOH$ molecules (GlH, AnH) coordinated with chromium may be joined to each other by means of hydrogen bridges between free carboxylic groups of molecules of amino-acids coordinated with different atoms of chromium. Increase in the number of GlH molecules coordinated with a chromium atom (for example, in the trichloride series from $[Cr(GlH)_4H_2OCl_3]$ to $[Cr(GlH)_5]Cl_3$) should increase the probability of formation of hydrogen bridges between molecules of the corresponding compounds. This is confirmed indirectly by the increase in the relative viscosity of the solutions (of the same molarity) of the compounds under comparison observed when successive inner sphere chlorine atoms or water molecules are replaced by GlH molecules (see vertical columns of Table 3).

TABLE 5

Time of dissolution	15-20 min	3 hours	1 day	8 days	75 days
Mol. wt.	2030	1040	520	377	316

We also think it quite possible that, in addition to association due to joining together of different molecules by hydrogen bridges, some molecules may be associated through glycine bridges which join chromium atoms belonging to different molecules, as follows:

$$[\cdots Cr\cdots NH_2CH_2COO-Cr\cdots-NH_2CH_2COO-Cr\cdots],$$
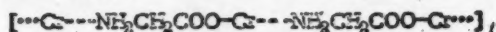
Such bridges might readily be formed in the following way. Molecules of water always enter the inner sphere of compounds in aqueous solution, and it is known that molecules of water coordinated with Cr^{+8} possess acidic properties, and are transformed into hydroxo-groups. The hydroxo-groups may react with GlH molecules coordinated with atoms of chromium belonging to other molecules, as follows:

$$[\cdots Cr\cdots GlH] + [HO-Cr\cdots] \longrightarrow [\cdots Cr\cdots Gl-Cr\cdots] + H_2O.$$

We suppose that it is in this way that unstable multi-nuclear complexes with glycine bridges are formed. Our study shows that all compounds containing glycine cycles can form multi-nuclear high molecular complexes without change in their empirical formula, i.e., they can form polymers. It is, however, evident that trichlorides of all series not containing glycine cycles cannot give rise to polymers with Gl bridges, and it is to this that we ascribe the fall in relative viscosity observed (see Table 3) in passing from dichlorides to trichlorides; trichlorides cannot form Gl bridges, although they are able to give rise to H bridges.

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ADDITION REACTIONS OF PERFLUORO - OLEFINS

I. L. Knunyants and A. V. Fokin

Tetrafluoroethylene, trifluoroethylene, and other fluoro-olefins have certain specific chemical properties, shown in their ability to take part in reactions which are not characteristic of olefins, and in their low reactivity in typically olefin reactions. Tetrafluoro- and trifluorochloro-ethylene readily add on alcohols in presence of alkaline catalysts, to give the corresponding ethers [1]; thus tetrafluoroethylene and ethanol readily yield 1,1,2,2-tetrafluorodiethyl ether. Ethylene and other olefins do not react with alcohols under these conditions.

Tetrafluoroethylene readily reacts with amines, giving probably as the primary product a 1,1,2,2-tetrafluoroethylamine derivative, which cannot be isolated due to its ready hydrolysis, with production of N-substituted difluoroacetamide [2,3,4]

$$CF_2{=}CF_2 + R_2NH \longrightarrow [HCF_2{-}CF_2NR_2] \longrightarrow HCF_2{-}C \underset{NR_2}{\overset{O}{\lessgtr}}$$
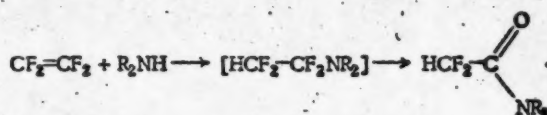
The reaction with ammonia proceeds similarly [4], giving difluoroacetonitrile, which polymerizes spontaneously to yield tri-(difluoromethyl)-triazine:

$$CF_2{=}CF_2 + NH_3 \longrightarrow [HCF_2{-}CF_2NH_2] \xrightarrow{-HF} [HCF_2{-}CN]_3.$$

Tetrafluoroethylene gives a number of products with sodium hydrogen sulfite [4], the most important being tetrafluoroethyl sulfonate and sodium difluoroacetate:

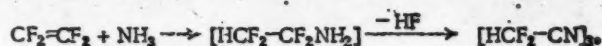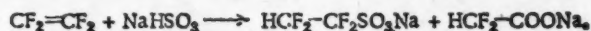$$CF_2{=}CF_2 + NaHSO_3 \longrightarrow HCF_2{-}CF_2SO_3Na + HCF_2{-}COONa.$$

Formation of difluoroacetic acid is ascribable to the mobility of fluorine atoms, which are readily eliminated from the a-carbon atom during hydrolysis

$$HCF_2{-}CF_2SO_3Na \xrightarrow{H_2O} [HCF_2{-}COSO_3Na] + 2HF \longrightarrow HCF_2{-}COONa + SO_2 + 2HF.$$
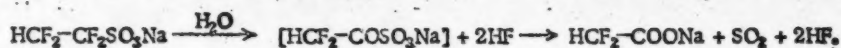
It is evident from the examples given that tetrafluoroethylene reacts readily with substances which are of the nature of nucleophil reagents.

The reactions are in many cases, such as those with primary and secondary amines, associated with evolution of heat, whereas the corresponding reactions either do not proceed at all with ethylene, or do so only with considerable difficulty. Addition of halogens or of hydrogen halides to fluoro-olefins takes place with much greater difficulty than to olefins.

Fluoro-olefins are distinguished by a strong tendency towards polymerization; perfluorochlorovinyl and, under certain conditions, tetrafluoroethylene polymerize spontaneously when stored, and cases of the almost explosive polymerization of fluoro-olefins are known. Not enough is known, however, of the reactions of polymerization of fluoro-olefins to enable us to speak more definitely of their mechanism.

It may be concluded that it is owing to the electronophilic nature of polyfluoro-olefins that reactions with nucleophil reagents may be realized by an ionic, rather than by a radical, mechanism. The addition of nucleophil reagents, which are donors of electrons, to fluoro-olefins is related to the very high electronegativity of fluorine, which attracts electrons from the carbon atoms of fluoro-olefins. This causes weakening of the π-bond of tetrafluoroethylene, which for this reason is not able to participate in the reactions of addition typical of olefins, and, on the contrary, acquires a special affinity for nucleophil reagents.

A comparison of the chemical properties of tetrafluoroethylene with those of ethylene strengthens our view regarding the differences between the π-bonds of these substances, resulting from modification of the electron density of the bonds. The fluoro-olefin molecule is an acceptor of electrons, whereas ordinary olefins are donors

thereof. It may in this connection be supposed that the initial process determining the reactions of tetrafluoro-ethylene is that of addition of the anion of the nucleophil reagent, which donates its electrons, and not the addition of cations, which is typical of reactions of addition to ethylene [5].
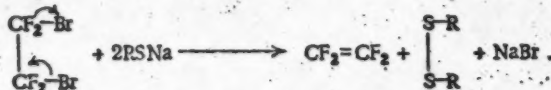
This supposition of addition of anions to tetrafluoroethylene is not without precedent; it is well known that compounds containing the carbonyl group (aldehydes, ketones) readily enter into reaction with nucleophil reagents, such as bisulfites, alcohols, ammonia, alkylamines, etc. These reactions begin with addition of anions to a carbon atom, functioning as a positive center [5].

The difficulty with which bromine adds on to tetrafluoroethylene (photo-activated reaction at 70-80°) is also ascribable to the special nature of its π-bond. As has been mentioned before, this circumstance is evidence of the attenuation of the π-bond in tetrafluoroethylene, and corresponds closely with the non-addition to tetra-phenylethylene of bromine under the ordinary conditions. The weakening of the bond in tetraphenylethylene is due basically to conjugation of the electrons of the double bond with those of the benzene rings, together with an inductional effect.
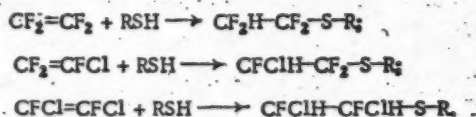
We have shown that the structural peculiarities of tetrafluoroethylene are reflected in the properties of the products of addition to it of halogens. The reaction between sulfhydryl compounds and 1:2-dibromotetra-fluoroethane or symmetrical difluorodichlorodibromoethane leads to regeneration of fluoro-olefins and to forma-tion of the appropriate disulfides. This reaction of oxidation of mercaptans is evidence of the lability of the bromine-carbon link in the 1:2-dibromotetrafluoroethane molecule, and may be explained on the basis of the above-described peculiarities of the structure of tetrafluoroethylene, which lead to the polarization of this bond

$$
\begin{array}{c}
CF_2\text{-Br} \\
| \\
CF_2\text{-Br}
\end{array}
+ 2RSNa \longrightarrow CF_2=CF_2 +
\begin{array}{c}
S\text{-R} \\
| \\
S\text{-R}
\end{array}
+ NaBr .
$$

The attenuation of the π-bond in perfluoro-olefins is the reason for the extreme instability of their dibro-mides, which are formed with difficulty, and which possess oxidative properties. Ethylene dibromide, on the contrary, reacts readily with mercaptans, with production of bisalkylethylene sulfides [6].

The powerful electronegative effect of fluorine is also frequently exerted on the π-bond; thus the C-C bond of hexafluoroethane is weakened as a result of abstraction of its electrons, and is broken by the action of bromine at raised temperatures, with production of two molecules of trifluorobromomethane [7]. This effect is closely analogous to the dissociation of hexaphenylethane, which contains six electron-attracting radicals. The affinity of fluorine for an electron is equal to 95 cal., and that of the phenyl group is much less, and if the dis-sociation were to be due to the induction effect only, hexaphenylethane would be expected to dissociate less readily than hexafluoroethane. In fact, however, hexaphenylethane dissociates more readily, since in the given case the effect of conjugation dominates.

A consideration of all these circumstances led us, in 1948 and 1949, to study the addition to fluoro-olefins of mercaptans, as typical nucleophil reagents. Various mercaptans reacted with tetrafluoroethylene, trifluorochlo-roethylene, or 1:1-difluoro-2:2-dichloroethylene in presence of alkaline catalysts, as follows:

$$CF_2=CF_2 + RSH \longrightarrow CF_2H\text{-}CF_2\text{-}S\text{-}R;$$

$$CF_2=CFCl + RSH \longrightarrow CFClH\text{-}CF_2\text{-}S\text{-}R;$$

$$CFCl=CFCl + RSH \longrightarrow CFClH\text{-}CFClH\text{-}S\text{-}R.$$

Of the three fluoro-olefins studied, the most reactive was found to be 1,1,2-trifluoro-2-chloroethylene (perfluorochlorovinyl). The high reactivity of $CF_2=CFCl$ is probably ascribable to the polarity of this reagent, since only such polarity, due to the asymmetrical structure of the molecule, could explain why addition of anions takes place preferentially at the carbon atom combined with fluorine only, i.e., at the atom with the smaller electron density. Similarly the products given by alkylamines with perfluorochlorovinyl are fluorochloroacetamides, not difluoroacetamides. As was expected, addition of ethylmercaptan to perfluorochlorovinyl does not take place in absence of catalysts or in presence of peroxides. In accordance with the views expressed above, addition takes place when the fluoro-olefin is heated under pressure with 3-5% of anhydrous sodium or potassium hydroxide, as catalyst.

Methyl, ethyl, and isopropyl mercaptan were thus made to react with perfluorochlorovinyl, to give methyl 1,1,2-trifluoro-2-chloroethyl sulfide, ethyl 1,1,2-trifluoro-2-chloroethyl sulfide, and 1,1,2-trifluoro-2-chloroethyl isopropyl sulfide, in 60-80% yields.

The sulfides so obtained were colorless, transparent, mobile liquids, with a characteristic unpleasant odor. Thiophenol reacts with perfluorochlorovinyl similarly to other mercaptans, giving phenyl 1,1,2-trifluoro-2-chloroethyl sulfide, in over 80% yield

$$CFCl=CF_2 + HS-C_6H_5 \longrightarrow CFClH-CF_2-S-C_6H_5.$$
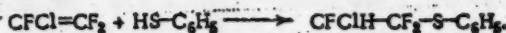
The sulfide so obtained was purified by fractional distillation; it had a pleasant odor, resembling that of the products of addition of thiophenol to olefins.

Some of the sulfides prepared by us were converted by elimination of hydrogen fluoride into fluorovinyl sulfides. Individual products could not be obtained by elimination of hydrogen fluoride with alcoholic alkali, in the usual way, and all attempts at separating the complex mixture of products so obtained were unsuccessful. The only substance isolated in a pure state was the product of addition of amyl alcohol to the vinyl derivative obtained by elimination of hydrogen fluoride.

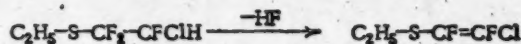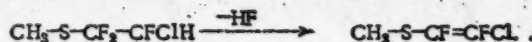Better results were obtained by heating the initial saturated sulfide with anhydrous alkali at 110-130°, simultaneously distilling off the unsaturated product. Thus 1,1,2-trifluoro-2-chloroethyl ethyl sulfide gave 1,2-difluoro-2-chlorovinyl ethyl sulfide , b.p. 106-107°, a colorless liquid with a characteristic odor, and methyl 1,1,2-trifluoro-2-chloroethyl sulfide afforded 1,2-difluoro-2-chlorovinyl methyl sulfide, a transparent liquid of b.p. 88-89°;

$$C_2H_5-S-CF_2-CFClH \xrightarrow{-HF} C_2H_5-S-CF=CFCl$$

and

$$CH_3-S-CF_2-CFClH \xrightarrow{-HF} CH_3-S-CF=CFCl .$$

The properties of the products obtained are given in Tables 1, 2 and 3.

EXPERIMENTAL

I. Methyl 1,1,2-trifluoro-2-chloroethyl sulfide. A mixture of 17 g of perfluorochlorovinyl, 8 g of methyl mercaptan, and 0.3 g of sodium hydroxide were heated for 6 hours at 115-125° in a stainless steel autoclave of 100 ml capacity. Unreacted olefin was distilled off, and the residue was washed with alkali and extracted with ether. The ethereal extract was distilled to remove solvent, and the residue was fractionally distilled, to give 10.6 g of pure product of b.p. 104°. Yield: 70% on reacted olefin.

The addition product, methyl 1,1,2-trifluoro-2-chloroethyl sulfide, is a transparent, mobile liquid with a specific odor. Analytical data, densities, and refractive indexes for this and other sulfides obtained similarly are given in Tables 1 and 2.

II. 1,2-Difluoro-2-chlorovinyl ethyl sulfide. A mixture of 10 g of ethyl 1,1,2-trifluoro-2-chloroethyl sulfide with 6.5 g of anhydrous potassium hydroxide is heated in a flask connected with a condenser, in an oil bath at 120-130°, collecting the unsaturated product of the reaction, which distils off at 105-107°. The distillate, after drying and redistillation, is 1,2-difluoro-2-chlorovinyl ethyl sulfide, b.p. 106-107°, a transparent, mobile liquid. Analytical and other data are given in Table 3.

III. Reaction of symmetrical tetrafluorodibromoethane or difluorodichlorodibromoethane with 2-hydroxyethyl mercaptan sodium salt.

1. Ten g of 2-hydroxyethyl mercaptan and 4.6 g of potassium hydroxide in 4 ml of water are placed in a round-bottomed flask fitted with a reflux condenser and a dropping funnel, and 13 g of warm symmetrical difluorodichlorodibromoethane (m.p. 34°) are added drop by drop. The addition of this substance is associated with considerable evolution of heat, with precipitation of KBr, and with copious evolution of a gas, which is condensed as a liquid in a receiver placed in a freezing mixture. After all of the dibromo-compound has been added the reaction mixture is heated for 1 hour at 60-65°. A total of 3.6 g of volatile liquid is collected in the receiver.

The residue in the flask is diluted with 30 ml of acetone, and is separated from the salt, the dry mass of which is 8.5 g. The acetone solution is dried with anhydrous magnesium sulfate, the acetone is distilled off, the residue is dissolved in chloroform, and the solution is treated with thionyl chloride. Excess of thionyl chloride and chloroform are distilled off, and the residue is fractionally distilled under reduced pressure. Four g of main fraction, b.p. 103-105°/2 mm, are obtained. The appearance and the characteristic odor of this product, as well as analytical and refraction data, show that it is identical with ethyl 2,2-dichloroethyl sulfide: d^{20} 1.341; n_D^{20} 1.5720, calculated MR_D 46.23, experimentally found MR_D 46.65 (previously described).

TABLE 1

Reagents		Addition product	Yield %	B.p. °C	d_4^t	n_D^t
Olefin	Mercaptan					
$CF_2=CFCl$	CH_3SH	$CH_3-S-C_2F_3ClH$	70	104	1.389/20°	1.4083/20°
Ditto	C_2H_5SH	$C_2H_5-S-C_2F_3ClH$	76-83	120/736	1.331/17°	1.4158/17°
"	$(CH_3)_2CHSH$	$(CH_3)_2CH-S-C_2F_3ClH$	74	135	1.275/20°	1.4178/20°
"	C_6H_5SH	$C_6H_5-S-C_2F_3ClH$	89	208	1.387/20°	1.5030/20°
$CF_2=CF_2$	CH_3SH	$CH_3-S-C_2F_4H$	75	63	1.322/8°	1.3675/8°
Ditto	C_2H_5SH	$C_2H_5-S-C_2F_4H$	60	88	1.246/18°	1.3735/18°
"	$(CH_3)_2CHSH$	$(CH_3)_2CH-S-C_2F_4H$	67	96	1.266/23°	1.3910/20°
"	C_6H_5SH	$C_6H_5-S-C_2F_4H$	76	64/12	1.3515/20°	1.4740/20°
$CFCl=CFCl$	CH_3SH	$CH_3-S-C_2Cl_2F_2H$	60	58.5/15	1.355/20°	1.5900/20°
Ditto	C_2H_5SH	$C_2H_5-S-C_2F_2Cl_2H$	62	138	1.425/20°	1.4612/20°
"	$(CH_3)_2CHSH$	$(CH_3)_2CH-S-C_2F_2Cl_2H$	52	159/738	1.302/25°	1.4534/20°
"	C_6H_5SH	$C_6H_5-S-C_2F_2Cl_2H$	78	93/3	1.400/20°	1.540/20°

NOTE: NaOH or KOH served as catalysts of the addition reactions. The duration of the addition reactions was from 3 to 6 hours.

TABLE 2

Formula	Mol. refraction		Sulfur, %		Fluorine, %		Chlorine, %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$CH_3-S-C_2F_3ClH$	28.47	29.14	19.50	20.09	34.55	34.05	21.57	22.18
$C_2H_5-S-C_2F_3ClH$	33.61	33.26	17.96	18.93	31.65	32.11	19.86	19.87
$(CH_3)_2CH-S-C_2F_3ClH$	37.72	38.03	16.55	16.80	29.60	29.03	18.41	18.66
$C_6H_5-S-C_2F_3ClH$	47.92	48.44	14.15	14.52	25.15	25.46	15.65	15.75
$CH_3-S-C_2F_4H$	23.77	23.96	21.62	22.04	51.35	51.14	—	—
$C_2H_5-S-C_2F_4H$	28.88	29.68	19.77	19.69	46.87	44.76	—	—
$(CH_3)_2CH-S-C_2F_4H$	32.90	33.30	18.10	18.32	43.00	43.26	—	—
$C_6H_5-S-C_2F_4H$	42.93	42.35	15.23	14.80	36.09	35.96	—	—
$CH_3-S-C_2F_2Cl_2H$	33.26	33.57	17.71	17.26	20.99	19.89	39.17	38.87
$C_2H_5-S-C_2F_2Cl_2H$	38.92	39.94	16.42	16.91	19.50	19.41	36.30	36.80
$(CH_3)_2CH-S-C_2F_2Cl_2H$	42.60	43.28	15.25	15.09	18.15	18.39	33.99	34.08
$C_6H_5-S-C_2F_2Cl_2H$	53.84	53.74	13.20	12.96	15.61	16.22	29.05	28.05
$C_2H_5-S-C_2F_2Cl$	32.65	32.58	20.21	19.81	23.97	24.94	22.36	21.70
$CH_3-S-C_2F_2Cl$	28.10	28.72	22.19	22.25	26.29	26.62	24.53	23.88
$CH_3-S-CFH-CFCl-O-C_5H_4$ . .	53.29	53.94	13.78	14.39	16.33	15.85	15.34	14.97

Found %: S 34.50; Cl 37.20.

$C_4H_6S_2Cl_2$. Calculated %: S 33.65; Cl 37.65

The volatile liquid collected in the receiver boiled at 22°, and was 1,2-difluoro-1,2-dichloroethylene. It was identified by treatment with bromine in a sealed steel cylinder at 50°, which gave a liquid product, most of which boiled at 42-45°/30 mm., and crystallized at 32-34°, mixed m.p. with difluorodichlorodibromoethane 34°.

Found %: F 12.98

$C_2F_2Br_2Cl_2$. Calculated %: F 13.33

2. Eight g of tetrafluoro-1,2-dibromoethane is added gradually to 11 g of 2-hydroxyethyl mercaptan and 5 g of potassium hydroxide in 5 ml of water. The reaction mixture becomes hot, and gas is evolved. The gas (1.6 l) is condensed in a freezing mixture, and the condensate is treated with bromine in a steel cylinder, for 1 hour at 80-90°. The oil so obtained boiled at 48°.

Found %: F 30.43
$C_2F_4Br_2$. Calculated %: F 29.32

The reaction product was separated from the potassium bromide formed, and was purified as in the preceding experiment. Vacuum fractionation gave a product of b.p. 102-105°/2 mm., the absence of fluorine from which, together with the analytical and refraction data obtained, and with its characteristic odor, suggests that it is the same disulfide as was obtained in the preceding experiment.

Found %: S 34.95; Cl 37.94
$C_4H_8S_2Cl_2$. Calculated %: S 34.50; Cl 37.30

Calculated MR_D 46.23; experimentally found MR_D 45.96.

TABLE 3

Initial sulfide	Product of elimination of hydrogen fluoride	Yield, %	B.p. °C	d^{20}	n_D^{20}
$C_2H_5-S-C_2F_3ClH$	$C_2H_5-S-CF=CFCl$	90	106-107	1.282	1.4385
$CH_3-S-C_2F_3ClH$	$CH_3-S-CF=CFCl$	57	88-89	1.324	1.4390
$CH_3-S-C_2F_3ClH$	$CH_3-S-CFH-CFCl-OC_5H_{11}$	–	73/3	1.190	1.4640

SUMMARY

1. It has been shown that, owing to the lowering of the electronic density of the π-bond of tetrafluoroethylene it assumes an electronphilic nature, as a result of which it readily adds on nucleophil agents, in particular mercaptans.

2. A series of new fluorine-containing sulfides have been obtained from addition of methyl, ethyl, and isopropyl mercaptans, and of thiophenol to tetrafluoroethylene, perfluorochlorovinyl, or symmetrical difluorodichloroethylene.

3. Elimination of hydrogen fluoride from the fluorochloro-sulfides gave alkyl fluorovinyl sulfides.

4. The reaction between tetrafluorodibromoethane and alkyl mercaptides involves the oxidation of the latter, with formation of disulfides and of tetrafluoroethylene.

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2-(2'-NAPHTHYL)-2-AMINOPROPIONIC ACID AND ITS PYRIMIDINE DERIVATIVES

PART 2

V. M. Rodionov and B. I. Kurtev

The corresponding ureido- or thioureido-derivatives are often prepared from β-amino-acids, for their identification. These derivatives readily eliminate one molecule of water, to give internal anhydrides, the so-called dihydro- or thiodihydrouracils:
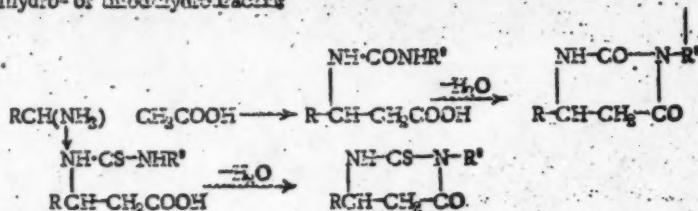

where R and R' = H, Alk, or Ar.

The ureido acids, dihydrouracils, and their sulfur-containing analogs are in most cases readily crystallizable substances, which are much less soluble in water than are the parent amino-acids. Very many of them possess specific biological activity, and their study is of considerable interest. Having previously prepared 2-(2'-naphthyl)-β-alanine in good yield [1], we have now prepared a number of pyrimidines characteristic of this substance.
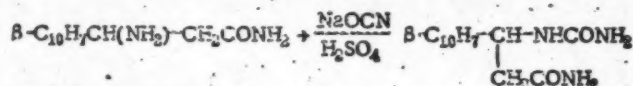
Three ureido-acids were synthesized, viz., 2-ureido-2-(2'-naphthyl)-propionic, 2-(ω-phenylureido)-2-(2'-naphthyl)-propionic, and 2-(N_2-methylureido)-2-(2'-naphthyl)-propionic acid, as starting products for the synthesis of the hexahydropyrimidines (dihydrouracils). The first of these substances was obtained in excellent yield by heating 2-naphthyl-β-alanine with urea in aqueous solution:

$$\beta\text{-}C_{10}H_7CH(NH_2)CH_2COOH + NH_2CONH_2 \longrightarrow \beta\text{-}C_{10}H_7CH(NHCONH_2)CH_2COONH_4.$$

It was found that the amide of the ureido acid was obtained as a by-product, in about 4% yield; its structure was established by hydrolyzing it to the free acid, and by converting it into naphthyldihydrouracil by heating the molten substance. Ammonia is evolved during this reaction:
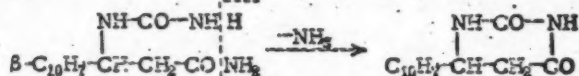
Formation of amides of β-ureido-acids from β-amino acids and urea has not till now been reported, and, in fact, there is no mention of any such amides in the literature. The amide was, for this reason, also synthesized from β-naphthyl-β-alanine and sodium cyanate, in the usual way:

$$\beta\text{-}C_{10}H_7CH(NH_2)\text{-}CH_2CONH_2 + \frac{NaOCN}{H_2SO_4} \quad \beta\text{-}C_{10}H_7\text{-}CH\text{-}NHCONH_2$$
$$CH_2CONH_2$$

β-(ω-phenylureido)-β-(β-naphthyl)propionic acid was prepared from β-naphthyl-β-alanine sodium salt and phenylisocyanate in aqueous solution:

$$C_{10}H_7CH(NH_2)CH_2COONa + C_6H_5NCO \longrightarrow C_{10}H_7CH(NHCONHC_6H_5)CH_2COONa.$$

β-(N_1-methylureido)-β-naphthylpropionic acid was prepared from β-naphthyl-N_1-methyl-β-alanine and sodium cyanate in boiling aqueous solution.

Conversion of the ureido acid and of N-methylureido acid into dihydrouracils is effected in good yield by boiling with dilute hydrochloric acid. Ring closure does not take place under these conditions with the ω-phenylureido acid, the reaction being one of full deamination, with formation of β-naphthylacrylic acid:

$$C_{10}H_7CH(NHCONHC_6H_5)CH_2COOH \longrightarrow C_{10}H_7CH=CH\cdot COOH.$$
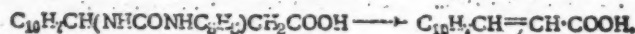
The appropriate phenylnaphthyldihydrouracil was prepared in small yield (30% of theory) by prolonged boiling of the phenylureido acid with dilute hydrochloric acid in methanol (10 parts by volume of 10% hydrochloric acid and 1 volume of methanol)

$$\underset{\underset{C_{10}H_7CH-CH_2-CO}{|}}{NH-CO---N\;H}\;\;C_6H_5\;\;\xrightarrow{-H_2O}\;\;\underset{\underset{C_{10}H_7CH-CH_2-CH}{|}}{NH-CO-N\cdot C_6H_5}$$
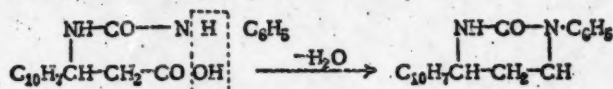
With stronger acid the sole reaction is methylation of the ureido acid. The tendency towards ring closure is lowered, and towards deamination raised, by attachment of a phenyl group to the nitrogen atom. Formation of β-naphthyldihydrothiouracil from β-naphthyl-β-alanine and potassium thiocyanate by heating with hydrochloric acid similarly takes place with considerable difficulty, the yield being less than 27%. The intermediate stage of formation of thioureid acid was not observed. The reaction proceeds as follows:

$$\underset{\underset{C_{10}H_2CH-CH_2-COOH}{|}}{NH_2}\;\xrightarrow{HSCN}\;\left[\underset{\underset{C_{10}H_7CH-CH_2-COOH}{|}}{NH-CS---NH_2}\right]\;\longrightarrow\;\underset{\underset{C_{10}H_7-CH-CH_2-CO}{|}}{NH-CS-NH}$$

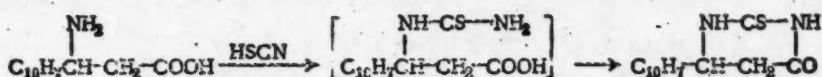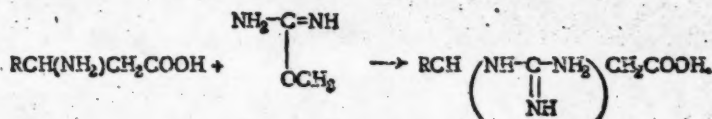The structure of 2-thio-6-naphthyl-dihydrouracil was confirmed by its desulfuration, to give naphthyldihydrouracil. An attempt to prepare naphthyl-N-methylthiodihydrouracil analogously from β-naphthyl-N-methyl-β-alanine was unsuccessful, as deamination takes place, and only naphthylacrylic acid was separated from the reaction product.
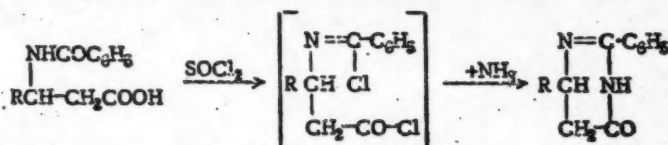
We have also investigated the possibility of preparation of amino (imino)-pyrimidines by ring closure of the appropriate guanidino acids. A number of methods of conversion of β-amino acids into β-guanidino acids have been studied in our laboratory, and we found, together with Urbanskaya [1], that the best method for preparation of β-guanidino derivatives is that based on the reaction between β-amino acids and O-methylisourea [1]:

$$RCH(NH_2)CH_2COOH\;+\;\underset{\underset{OCH_3}{|}}{NH_2-C=NH}\;\longrightarrow\;RCH\left(\underset{\underset{NH}{||}}{NH-C-NH_2}\right)CH_2COOH.$$

Guanidination of β-(β-naphthyl)-β-alanine takes place with difficulty, the yield not exceeding 15%. This result is closely connected with Urbanskaya's earlier observation that β-amino acids with aliphatic radicals substituted in the β-position are more readily guanidinated than where the substituent is a phenyl group, and that the reaction proceeds the more readily the smaller is the molecular weight of the alkyl radical. The high molecular weight of the naphthyl radical leads to a reduction in the yield, to 15%.

Ring closure of guanidinonaphthylpropionic acid does not take place at all, the reaction being one of deamination with production of naphthylacrylic acid.

Zvorykina [2] has shown in an earlier paper from our laboratory that the amides of acyl derivatives of β-amino acids readily afford tetrahydropyrimidines by the following reactions:

$$\underset{\underset{RCH-CH_2COOH}{|}}{NHCOC_6H_5}\;\xrightarrow{SOCl_2}\;\left[\underset{\underset{CH_2-CO-Cl}{|}}{\overset{N==C-C_6H_5}{\underset{|}{RCH\;Cl}}}\right]\;\xrightarrow{+NH_3}\;\underset{\underset{CH_2-CO}{|}}{\overset{N==C-C_6H_5}{\underset{|}{RCH\;NH}}}$$

This reaction was performed with N-acetyl-β-naphthyl-β-alanine, giving 4-oxo-1-(β-naphthyl)-2-methyl-3,4,5,6-tetrahydropyrimidine.

The ureido acids and pyrimidine derivatives synthesized are given in the following Table.

EXPERIMENTAL

β-Ureido-β-(β-naphthyl)-propionic acid. 2.15 g of finely powdered β-(β-naphthyl)-β-alanine, 8 g of urea, and 45 ml of water are heated on a boiling water bath for 15 hours. The substrates gradually pass into solution, and after 2 hrs. the reaction mixture is a slightly turbid solution with a strongly ammoniacal odor. After cooling, 10 ml of 4% aqueous alkali should be added, in order to prevent possible premature separation of the ureido acid. The solution is filtered, in order to remove the insoluble residue which usually forms. The filtrate

TABLE

Formula and name	Yield %	M.p. of pure substance, °C
$C_{10}H_7CH(NHCONH_2)CH_2COOH$ β-Ureido-β-(β-naphthyl)-propionic acid	92.5	199-199.5 with foaming
$C_{10}H_7CH(NHCONH_2)CH_2CONH_2$ β-Ureido-β-(β-naphthyl)-propionamide	80	217.5 with decomposition
NH—CO | | CO CH₂ | | NH—CH·C₁₀H₇ 6-(β-naphthyl)-dihydrouracil	73	245-246
$C_{10}H_7CH(NHCONHC_6H_5)CH_2COOH$ β-(ω-Phenylureido)-β-(β-naphthyl)-propionic acid.	87	178.5-179.5 with foaming
$C_{10}H_7CH(NH \cdot CONHC_6H_5)CH_2COOCH_3$ Methyl β-(ω-phenylureido)-β-(β-naphthyl)-propionate	89.5	142-143
C₆H₅NH—CO | | CO CH₂ | | NH CH—C₁₀H₇ 3-Phenyl-6-(β-naphthyl)-dihydrouracil	30	233-234
$C_{10}H_7CH(N—CONH_2)CH_2COOH$ CH₃ β-N-Methylureido-β-(β′-naphthyl)-propionic acid	30	180-181 with foaming

NH—CO
     | |
     CO—CH₂
     | |
 CH₃N—CHC₁₀H₇
 6-(β′-Naphthyl)-1-methyldihydrouracil . . . .
	70	200.5-201.5

NH—CO
     | |
     CS   CH₂
     | |
    NH—CH·C₁₀H₇
 β-Thio-6-(β′-naphthyl)-dihydrouracil . . . .
	27	261-261.5

$C_{10}H_7CH(NH—C—NH_2)CH_2COOH$
          ‖
         NH
 β-Guanidino-β-(β-naphthyl)-propionic acid. . . . .
	15	249-250

NH—CO
     | |
 CH₃C   CH₂
     ‖ |
     N—CH·C₁₀H₇
 4-Oxo-6-(β-naphthyl)-2-methyl-3,4,5,6-tetrahydropyrimidine . . . . . .
	59.5	127.5-129

is extracted a few times with ether, and the aqueous residue is made acid to Congo red with hydrochloric acid. The voluminous precipitate is collected on the filter pump, washed with water, and dried on a porous tile and then in an oven at 70°. The yield is 2.38 g (about 92.5% of theoretical), and the product melts at 196-197°, with foaming. The dry product is recrystallized from alcohol, when the m.p. rises to 199-199.5°, with characteristic foaming. The ureido acid is not soluble in ether, benzene, or cold water, slightly soluble in boiling water, rather more soluble in cold concentrated hydrochloric acid, and readily soluble in dilute alkalis. It is difficultly soluble in cold methanol or ethanol, but very soluble in the boiling solvents; solubilities in acetone are similar, but somewhat lower.

Found %: C 64.89; 65.14; H 5.19; 5.28; N 10.48; 10.45.
$C_{14}H_{14}O_3N_2$. Calculated %: C 65.4; H 5.42; N 10.85.

The residue obtained by filtration of the alkalized reaction solution is dissolved in boiling alcohol, and the solution is filtered while hot from insoluble impurities. Silky colorless crystals separate from the filtrate on cooling; the yield is 0.11 g (4.2% of theoretical), m.p. 213.5° (with decomposition). The properties of this product, and the analytical data obtained for it show that it is β-ureido-β-(β-naphthyl)-propionamide.

When heated with aqueous alkali the substance dissolves readily, with evolution of ammonia, and addition of acid to the cooled solution causes precipitation of a compound of m.p. 196-197° (with foaming), which does not depress the m.p. of β-ureido-β-(β-naphthyl)-propionic acid. The substance evolves ammonia when heated at the m.p. in a test-tube, and the molten product rapidly crystallizes. The solid so obtained is recrystallized from alcohol, to give a product of m.p. 244-245°, mixed m.p. with pure 6-(β-naphthyl)-dihydrouracil 245°. The substance does not depress the m.p. of β-ureido-β-(β-naphthyl)-propionamide, prepared from the amide of β-(β-naphthyl)-β-alanine and sodium cyanate.

Found %: C 65.59; 65.72; H 5.81; 5.64; N 16.29; 16.47.
$C_{14}H_{15}O_2N_3$. Calculated %: C 65.37; H 5.83; N 16.34.

β-Ureido-β-(β-naphthyl)-propionamide. A solution of 0.215 g of the amide of β-(β-naphthyl)-β-alanine and 0.072 g of sodium cyanate in 7.6 ml of about 2% sulfuric acid is heated for 5-10 min. on a boiling water bath, and the crystalline precipitate separating from the cooled solution is collected on the filter pump. The yield of product, m.p. 216°, is 0.20 g, i.e., about 80% of theoretical. All the properties of the product coincide with those of the amide obtained as a by-product of the synthesis of β-ureido-β-(β-naphthyl)-propionic acid.

β-(ω-phenylureido)-β-(β-naphthyl)-propionic acid. Phenylisocyanate (0.68 g) is added drop by drop, with constant stirring, and cooling the reaction vessel with ice, to a solution of 1.08 g of β-(β-naphthyl)-β-alanine in 10 ml of 4% aqueous sodium hydroxide. After a few hours the reaction mixture is diluted with water and filtered. The filtrate is extracted with ether, and is made acid with dilute hydrochloric acid. The oily precipitate separating solidifies after a few hours, when it is collected, washed and dried at 70°. The yield of product, m.p. 160.5-170.5° (with foaming), is 1.45 g (87% of theoretical); after crystallization from aqueous alcohol and then from alcohol alone the m.p. rises to 178.5-179.5° (with foaming). The substance crystallizes in colorless prisms, and is insoluble in ether or benzene, fairly soluble in cold alcohol or acetone, and very soluble in hot alcohol or acetone. It is insoluble in water or mineral acids, and is readily soluble in aqueous alkalis.

Found %: N 8.73; 8.81.
$C_{20}H_{18}O_3N_2$. Calculated %: N 8.38.

β-(N_1-methylureido)-β-(β-naphthyl)-propionic acid. A mixture of 0.38 g of β-(β-naphthyl)-β-N-methylalanine and 0.20 g of sodium cyanate (85% excess) in 10 ml of water is heated for 4 hours on a boiling water bath. The cooled solution is filtered, and dilute hydrochloric acid is added to a strongly acid reaction to Congo red. The voluminous precipitate is collected, washed with water, and dried first on a porous tile and then in an oven at 70°; yield 0.32 g (about 72% of theoretical). After two recrystallizations from alcohol the substance has m.p. 180-181°; it is sparingly soluble in cold alcohol or acetone, but more soluble in the hot solvents, insoluble in ether, benzene, water, or mineral acids, and readily soluble in aqueous alkalis.

Found % : N 10.28; 10.34.
$C_{15}H_{16}O_3N_2$. Calculated %: N 10.29.

6-(β-Naphthyl)-dihydrouracil. A solution of 2.58 g of β-ureido-β-(β-naphthyl)-propionic acid in 100 ml of concentrated hydrochloric acid (d 1.18) is boiled for 30 min., the precipitate which separates from the cooled

solution is collected, washed with water, and dried at 70°. The product, weighing 2.33 g, and melting indefinitely at 225-234°, is treated with boiling ethanol (50 ml), the suspension is filtered hot, and the residue is washed on the filter with two further small portions of hot ethanol; the m.p. is thus raised to 244-245°. After one more recrystallization from a large volume of alcohol 1.10 g of analytically pure product are obtained, m.p. 245-246°; the alcoholic filtrate yields a further 0.55 g of this substance. The total yield is 1.65 g, i.e., 73% of theoretical.

Naphthyldihydrouracil crystallizes in small colorless prisms, often joined in rosettes. It is sparingly soluble in the ordinary organic solvents, not very soluble in boiling alcohol, and insoluble in water or mineral acids. It is fairly readily hydrolyzed by boiling 4-5% aqueous alkalis, to ureidonaphthylpropionic acid

Found % : C 70.20; H 4.48; N 12.04, 12.12·
$C_{14}H_{12}O_2N_2$. Calculated %: C 70; H 5.0; N 11.66.

Attempted ring closure of β-(ω-phenylureido)-β-(β-naphthyl)-2-propionic acid.

1. Boiling the phenylureido-naphthyl-propionic acid with hydrochloric acid gives β-(β-naphthyl)-acrylic acid in practically theoretical yield.

2. Boiling with hydrochloric acid and methanol leads to formation of methyl-β-(ω-phenylureido)-β-(β-naphthyl)-2-propionate.

A mixture of 0.66 g of β-phenylureido-β-naphthylpropionic acid, 20 ml of methanol, and 5 ml of concentrated hydrochloric acid (d 1.18) is boiled for 5 hours on a water bath, the solution is cooled, and water is added. The precipitate separating is collected after 3 hours, washed with water, and dried at 70-80°; yield 0.66 g of substance of m.p. 136.5-140.5° (about 89.5% of theoretical). After recrystallization from aqueous alcohol the m.p. rises to 142-143°.

The methyl ester crystallizes from aqueous alcohol in the form of colorless prisms, insoluble in water, alkalis, or acids, readily soluble in acetone, sparingly soluble in cold, but readily soluble in hot, benzene or alcohol, and sparingly soluble in ether. It is rapidly hydrolyzed by dilute alkalis to the corresponding acid.

Found %: C 74.42; 72.34; H 5.66; 5.73; N 7.81; 7.83·
$C_{21}H_{20}O_3N_2$. Calculated %: C 73.39; H 5.75; N 8.04.

3. Preparation of 3-phenyl-6-(β-naphthyl)-dihydrouracil. A mixture of 1.67 g of β-(ω-phenylureido)-β-(β-naphthyl)-propionic acid, 100 ml of 16% hydrochloric acid, and 10 ml of methanol is boiled for 15-20 hrs. on the water bath. Visible dissolution of the initial acid is not observed. The cooled reaction mixture is filtered, giving a residue of 1.12 g of a substance, m.p. 182-207°, which is dissolved in a large volume of boiling alcohol. The solution on cooling deposits 0.47 g of crystalline product (30% of theoretical yield), m.p. 232-233°, raised by repeated crystallization to 233-234°.

3-Phenyl-6-(β-naphthyl)-dihydrouracil crystallizes in short colorless prisms. It is difficultly soluble in water, alkalis, acids, ether, benzene, and cold alcohol, and sparingly soluble in boiling alcohol. It is readily hydrolyzed by boiling dilute alkalis to phenylureidonaphthylpropionic acid.

Found %: C 75.63; 75.57; H 5.31; 5.13; N 8.99 .
$C_{20}H_{16}O_2N_2$. Calculated %: C 75.92; H 5.10; N 8.88

6-(β-naphthyl)-1-methyldihydrouracil.
A suspension of 0.54 g of β-(N-methylureido)-β-(β-naphthyl)-propionic acid in 24 ml of dilute hydrochloric acid (1:1) is heated for 90 minutes on a boiling water bath; dissolution of the substance is not seen to take place. The cooled suspension is filtered, and the residue is washed with water and dried at 100°. The yield of crude product, m.p. 190-195°, is 0.5 g; the m.p. rises to 196-199° after one recrystallization from alcohol, and further purification is effected by dissolving in boiling alcohol, and adding two volumes of ether, when 0.38 g (70% of theoretical) of pure product, m.p. 200.5-201.5°, separates.

6-(β-Naphthyl)-1-methyldihydrouracil crystallizes in thick prisms. It is insoluble in cold, and slightly soluble in hot, water, and is more soluble in alcohol than in water, and even more so in acetone. It is insoluble in ether. The substance is rapidly hydrolyzed by hot alkalis.

Found % : C 71.07; 71.26; H 5.57; 5.61; N 11.09; 11.29.
$C_{15}H_{14}O_2N_2$. Calculated %: C 70.85; H 5.55; N 11.02.

2-Thio-6-(β-naphthyl)-dihydrouracil. A mixture of 2.15 g of L-(β-naphthyl)-β-alanine, 1.52 g of potassium thiocyanate, and 1 ml of concentrated hydrochloric acid in 15 ml of water is evaporated to dryness on a water bath, and the powdered residue is heated on the oil bath at 145-150° for 2-3 hrs. The cooled product is heated for 10 min at 100° with 20 ml of 4% hydrochloric acid, and the residue is collected, washed with water, and dried. The product, weighing 1.72 g, melts at 144-197° (with partial decomposition at about 160°). Neutralization of the filtrate with sodium acetate gives 0.38 g (17.7% of the weight of β-naphthyl-β-alanine taken) of unreacted initial substance.

The product of m.p. 144-197° is dissolved in 130 ml of boiling alcohol, and the solution is cooled, when a substance containing sulfur and nitrogen separates, m.p. 239-241.5°, yield 0.57 g, i.e. 22% on total, or 27% on reacted, naphthyl-β-alanine. Repeated recrystallizations finally gave a product of m.p. 261-262.5°, analysis of which showed that it is still not quite pure.

Found % : N 10.52; 10.56; S 11.81; 12.01
$C_{14}H_{12}ON_2S$, Calculated %: N 10.93;   S 12.51

2-Thio-6(β-naphthyl)-dihydrouracil is insoluble in ether or benzene, sparingly soluble in cold alcohol or acetone, and readily soluble in hot alcohol and acetone. It is insoluble in water or mineral acids, but is easily dissolved without decomposition in alkaline solutions.

Conversion into 6-(β-naphthyl)-dihydrouracil. A small amount of 2-thio-6-(β-naphthyl)-dihydrouracil is heated for 25 hrs. with a large excess of lead acetate in aqueous alcoholic solution, after which the alcohol and some of the water are distilled off, and the cooled residual solution is filtered. The black residue on the filter is repeatedly extracted with small amounts of boiling alcohol, and the combined extracts are stood for 24 hours, to give a deposit of small prisms, joined in rosettes, of m.p. 245-246", not depressing the m.p. of a sample of 6-β-naphthyl-dihydrouracil, prepared by a different method, but giving a considerable depression of the m.p. of 2-thio-6-β-naphthyl-dihydrouracil, to 220°.

All attempts at preparing 2-thio-6(β-naphthyl)-1-methyl-dihydrouracil by a similar method were unsuccessful, the deamination produce β-(β-naphthyl)-acrylic acid being obtained in all cases.

β-Guanidino-β-(β-naphthyl)-propionic acid. A solution of 5.94 g of O-methylisourea hydrochloride (m.p. 117-118°) in 30 ml of anhydrous methanol is cooled in a freezing mixture, and added to a similarly cooled solution of 1.35 g sodium in 30 ml anhydrous methanol. The sodium chloride separating out after 15 minutes is filtered off, and is washed with cooled anhydrous methanol. The clear solution of O-methylisourea so obtained is added to 6.45 g of finely powdered β-(β-naphthyl)-β-alanine, followed by 50 ml of water and about 300 ml methanol, with mechanical stirring. The reaction proceeds very slowly, the β-amino acid does not dissolve for a long time, and the solution is stirred mechanically for 15 days. The methanol is then distilled off under reduced pressure, on a water bath at 40-50°. The first parts of the distillate have a strong ammonia odor. The precipitate separating after elimination of methanol is collected after a day, and washed with small amounts of water; the yield is 1.27 g, m.p. 233-236° (with decomposition). A small amount of substance of m.p. 126.5-129.5° separated from the filtrate on the following day; the amount was too small to permit of its examination. The product, of m.p. 233-236°, is dissolved in dilute hydrochloric acid, the solution is extracted several times with ether, and excess of concentrated ammonia is added. The precipitate forming is collected and washed with water; yield 1.17 g (about 15% of theoretical), m.p. 239-240° (with decomposition), rising to 249-250° (with decomposition). when recrystallized from aqueous alcohol. β-Guanidino-β-(β-naphthyl)-propionic acid, is a finely crystalline powder readily soluble in cold dilute acids and in boiling aqueous alcohol, but difficultly soluble in cold water and alcohol.

Found %: N 16.46; 16.25; 16.34.
$C_{14}H_{15}O_2N_3$ Calculated %: N 16.33

All attempts towards the cyclization of guanidinonaphthylpropionic acid were unsuccessful, as deamination took place when it was heated with hydrochloric acid, to give β-naphthylacrylic acid in good yield.

4-Oxo-6-(β-naphthyl)-2-methyl-3,4,5,6-tetrahydropyrimidine. A mixture of 1.28 g of N-acetyl-β-(β-naphthyl)-β-alanine (m.p. 226-228°, with 8 ml of acetic anhydride is heated for 3 hrs on an oil bath at 140°. The excess of acetic anhydride is distilled off under reduced pressure on an oil bath at about 130°, the last traces being decomposed by boiling with 25 ml of water for 20-30 min.; a small amount of crystalline material separates from the aqueous solution on cooling. The oily residue in the flask is extracted with a small amount of benzene, after which it crystallizes. The crystalline product, together with that separating from the aqueous solution, is wetted with alcohol and is shaken for 1 hour with 10 ml of cold 2% alkali. The insoluble residue is collected on a filter, washed with water, and dried. The yield is 0.71 g (59-60% of theoretical) of

substance of m.p. 124-126°, raised to 127.5-128° by recrystallization from water.

4-Oxo-6-(β-naphthyl)-2-methyl-3,4,5,6-tetrahydropyrimidine crystallizes from water as needles. It is very soluble in alcohol, chloroform, or hot benzene, and fairly soluble in cold ether or benzene. It is very soluble in concentrated, but only sparingly soluble in dilute, hydrochloric acid or in aqueous alkali at room temperature. When recrystallized from water it retains it tenaciously, and requires prolonged drying in a desiccator before being analyzed.

Found %: C 75.57; 75.40; H 6.08, 6.22; N 11.89; 11.93.
$C_{15}H_{14}ON_2$. Calculated %: C 75.60; H 5.92; N 11.76.

The alkaline filtrate obtained during purification of the product was made acid with dilute hydrochloric acid, when 0.02 g of the initial N-acetyl-β-(β-naphthyl)-β-alanine separated out.

SUMMARY

1. β-Ureido-β-(β-naphthyl)-propionic acid, β-(ω-phenylureido)-β-(β-naphthyl)-propionic acid, and β-(N_1-methylureido)-β-(β-naphthyl)-propionic acid have been prepared, and have been converted into the corresponding 2,4-dioxo-hexahydropyrimidine derivatives 6-(β-naphthyl)-dihydrouracil, 3-phenyl-6-(β-naphthyl)-dihydrouracil, and 6-(β-naphthyl)-1-methyl-dihydrouracil.

2. Its amide was formed as a by-product of preparation of β-ureido-β-(β-naphthyl)-propionic acid, and was also synthesized from β-amino-β-(β-naphthyl)-propionic acid and sodium cyanate.

3. β-Ureido-β-(β-naphthyl)-propionamide undergoes cyclization when heated.

4. Methyl-β-(ω-phenylureido)-β-(β-naphthyl)-propionate has been prepared.

5. 2-Thio-6-(β-naphthyl)-dihydrouracil, β-guanidino-β-(β-naphthyl)-propionic acid, and 4-oxo-6-(β-naphthyl)-2-methyl-3,4,5,6-tetrahydropyrimidine have been synthesized.

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See Consultants Bureau English translation, p. 123.

SYNTHESIS OF β-AMINO-β-CYCLOHEXYLPROPIONIC ACID AND OF SOME OF ITS DERIVATIVES

V. M. Rodionov and T. S. Kiseleva

The method of synthesis of β-amino acids discovered in our laboratory in 1926, depending on condensation of aromatic aldehydes with malonic acid in presence of alcoholic ammonia [1], has recently been extended to aldehydes of the aliphatic and naphthalene series [2], and preliminary experiments have been made on its application to heterocyclic aldehydes [3]. It was for certain reasons of importance to extend the method to aldehydes of the cyclane group. The synthesis of β-amino acids with cyclic substituents in the β-position would be of interest not only for merely preparative reasons.

We have, together with Zvorykina [4], shown that β-aminopelargonic acid (β-hexyl-β-alanine) is a biologically active substance, which similarly to β-alanine, although to a much smaller degree, stimulates the growth of yeast. A particularly interesting biologically active substance, possessing biotin activity, is hexylglyoxalidone (I), which is easily prepared from β-aminopelargonamide by the Hoffman reaction. The structure of this substance is very similar to that of desthiobiotin (II), a degradation product of the universal growth factor biotin (III).
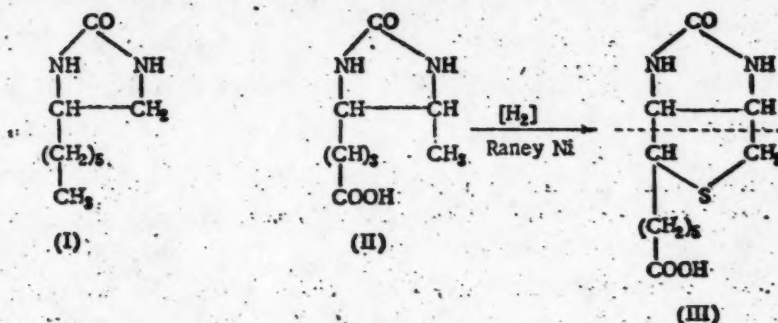

The glyoxalidone ring is seen to be a part of the molecule of these three biologically active substances, and it seems that the activity of these compounds depends largely on the presence of this heterocyclic system, since desthiobiotin (II) differs very little from biotin in its activity, which is also little affected by methylating the carboxylic group. This activity requires the presence in position 4(5) of the ring of a C_6 substituent. However, replacement of hexyl by phenyl leads to total loss of biotin activity, as was shown by a microbiological study of phenylglyoxalidone, prepared in 1932 by Kanevskaya [5].

It was of very great interest to find what is the effect of substituting cyclohexyl for phenyl in both β-aminopropionic acid and in the corresponding glyoxalidone derivative, for the preparation of which it was necessary to study the Hoffmann reaction with β-cyclohexyl-β-alanine.
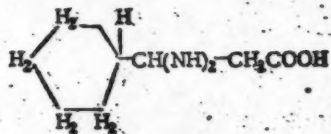
We have since 1943 been conducting in our laboratory a systematic study of the reaction between acylated amides of β-amino acids and hypobromite, from which it appears that the chief product of the reaction is a 4(5)-substituted glyoxalidone, formed through the intermediate stage of acylglyoxalidone, first isolated by Zvorykina [4]: (see top of next page). The study of cyclohexyl-β-aminopropionic acid is thus of interest both for confirmation of the mechanism of formation of 4(5)-glyoxalidone derivatives, and for the elucidation of the biological activity of the acid itself and of the derived cyclohexylglyoxalidone.
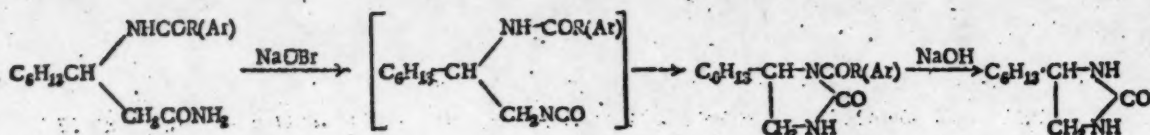
In order to prepare β-amino-β-cyclohexylpropionic acid by our method it was first necessary to work out a convenient method for preparation of hexahydrobenzaldehyde. A number of published methods were tested, and it was found that the best results were given by that involving decomposition of the ester obtained from monochloroacetic ester and cyclohexanone [6].
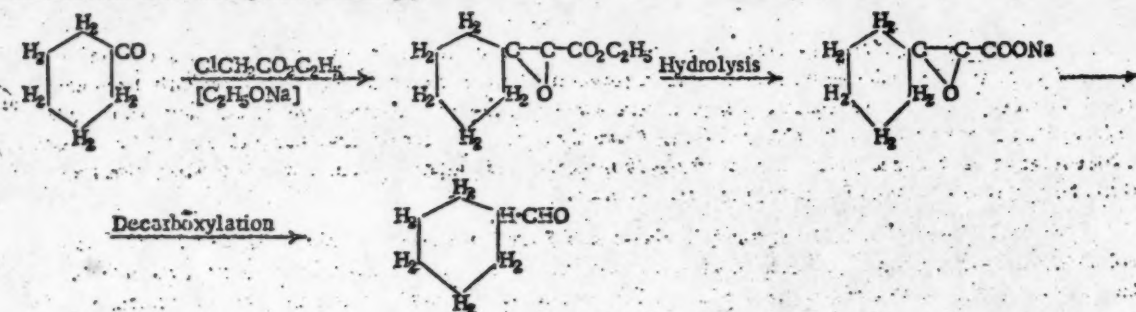

Hexahydrobenzaldehyde was obtained by us as the crystalline aldehyde-ammonia derivative of m.p. 104-105° (see experimental part). The same reaction was applied to cyclopentanone, and cyclopentylformaldehyde was obtained in somewhat lower yield.

Condensation with malonic acid was at first done in the ordinary way. Alcoholic ammonia was added to hexahydrobenzaldehyde, and the crystalline aldehyde-ammonia separating out was heated with malonic acid. The ammonia solution was taken in 10% excess of the theoretical amount of NH_3 required for the reaction. The yield of β-amino acid amounted to 50% of theory. Better yields were obtained when the excess of alcoholic ammonia,, with absolute alcohol as the solvent, was added to the crystalline aldehyde-ammonia compound. Very good results were obtained taking a 40% excess of ammonia, and heating for 8 hours on the water bath. Under these conditions the yield of amino acid was raised to 66% , and the yield of unsaturated acid obtained as a by-product was reduced to 11% of theoretical.

The reaction of condensation of hexahydrobenzaldehyde with malonic acid differs from that with aromatic aldehydes in that two isomeric unsaturated acids are obtained, one with the double bond in the α-β-position (cyclohexylacrylic acid, $C_6H_{11}CH=CH\cdot COOH$), and the second with a γ-double bond (cyclohexylidenepropionic acid, $C_6H_{10}=CH\cdot CH_2COOH$). The unsaturated acid separated by us was completely identical · i with cyclohexylacrylic acid, described in 1928 by Sircar [7] and by Venus-Danilova [8] in 1934.

The N-acetyl-, N-benzoyl-, and N-carbomethoxy-derivatives of β-amino-β-cyclohexylpropionic acid, and their amides, were prepared, and the Hoffmann reaction was carried out with all of these acylated amides. The N-benzoyl and N-carbomethoxy amides gave cyclohexylglyoxalidone, together with its N-benzoyl or N-carbomethoxy derivative; this affords further confirmation of the mechanism proposed by us for the Hoffmann reaction with β-amino acids [4]. β-Acetamido-β-cyclohexylpropionamide under the same conditions gives only cyclohexylglyoxalidone, however. β-Ureido-β-cyclohexylpropionic acid was also synthesized, and the appropriate cyclohexyldihydrouracil was prepared from it.
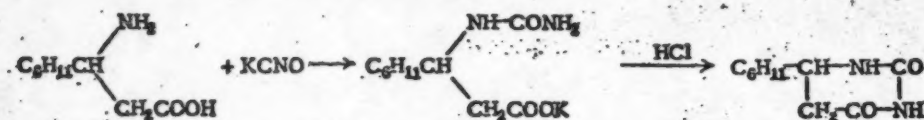

EXPERIMENTAL

Preparation of cyclohexylglycidic ester. Into a three-necked flask fitted with a stirrer, a reflux condenser, and a thermometer are placed 49 g of cyclohexanone ($\frac{1}{2}$ mole), 61 g of ethyl monochloroacetate, and 100 ml of dry benzene; the mixture is cooled to 0°, and sodium ethoxide powder is added in small

portions*, from a sealed extension connected with the flask by rubber tubing; the rate of addition of sodium ethoxide is regulated by the temperature of the reaction mixture, which should not exceed 15°. After the whole of the sodium ethoxide has been added, the contents of the flask are stirred for 4 hrs., and are allowed to stand for 48 hrs. at room temperature, when the flask is placed on a boiling water bath, and the mixture is diluted with water. A benzene solution of the glycidic ester separates. The lower, aqueous layer is twice extracted with benzene, and the combined benzene extracts are washed successively with water, with 3% acetic acid, and again with water, and are then dried with anhydrous sodium sulfate. After distilling off the benzene, the residual glycidic ester is fractionally vacuum distilled, collecting the fraction boiling at 115-116°/10 mm; yield 67 g, i.e., 73% of theoretical. The reaction proceeded much faster when sodamide was substituted for sodium ethoxide, but the yield fell to 50%.

Hydrolysis of the cyclohexylglycidic ester. 67 g of ester are added gradually to a solution obtained by adding 9.2 g of sodium to 220 ml of absolute alcohol. The slightly turbid solution is cooled to 15°, and 8 ml of water is added, causing considerable heating, and being followed by precipitation of sodium salt of glycidic acid. The precipitate is collected on the next day, and washed with 30 ml of absolute alcohol followed by 30 ml of ether, and dried at 120°; yield 57.6 g, i.e., about 90% of theoretical.

Preparation of hexahydrobenzaldehyde, and its conversion into aldehyde-ammonia compound. This stage of the synthesis, viz., separation of aldehyde obtained by decomposition of glycid salt

$$C_6H_{10}-CH \cdot COONa \xrightarrow{H_2SO_4} C_6H_{10}CHO + CO_2$$
$$\underset{O}{\diagdown\diagup}$$
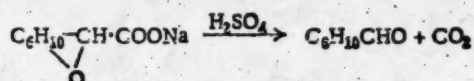
is the most difficult, since the free aldehyde readily polymerizes on standing, and is very quickly converted in the presence of mineral acids into crystalline metahexahydrobenzaldehyde [9]. The following procedure was designed to prevent this undesirable reaction: sulfuric acid was taken instead of the usual hydrochloric acid, and was added gradually to the sodium salt of the glycidic acid, in a current of steam. The hexahydrobenzaldehyde was thus removed from the acid medium as soon as it was formed, so greatly reducing polymerization.

A solution of 250 g of sodium salt of the glycidic acid in 150 ml of water is placed in a three-necked flask, and 150 ml of 1:1 sulfuric acid is added gradually through a dropping-funnel, steam being passed through the solution at the same time. The hexahydrobenzaldehyde distilling over is collected in ice-water, the upper layer is collected, dissolved in 50 ml of alcohol, and the solution is saturated with ammonia, with violent shaking and good cooling. The crystalline aldehyde-ammonia compound separating is left with the ammoniacal solution for 10-12 hrs, after which it is collected, washed with small portions of alcohol, and dried on a porous tile, and then in a vacuum desiccator; yield of aldehyde-ammonia compound, m.p. 104-105°, 47.7 g, a further 4 g of which was obtained by evaporating the alcoholic mother liquor under reduced pressure. The aqueous condensate (800 ml) is redistilled giving 300 ml of distillate containing aldehyde, from which a further 13.5 g of aldehyde-ammonia, m.p. 103-104°, is obtained. The total yield is 65.2 g, or about 42% of theoretical.

The compound so obtained does not contain oxygen, and its analysis gives the formula $(C_7H_{13}N)_x$, i.e., it is an aldimine. It crystallizes in bundles of thin needles, melting at 104-105°, with decomposition. It is readily soluble in benzene (1:6) sparingly soluble in ether, and practically insoluble in water. At room temperature 0.1 g of the aldimine does not dissolve in 10 ml of alcohol, but it passes into solution at 60°, not crystallizing out again, however, when the solution is cooled; the aldimine evidently decomposes when heated, to yield free aldehyde. This view is confirmed by the observation that when the cooled alcoholic solution is again saturated with ammonia it gives a precipitate of the same aldimine crystals, m.p. 104-105° (after drying). This behavior of the aldimine was used for its purification by recrystallization.

Found % : C 75.31; 75.21; H 11.85; 11.88; N 12.71; 12.75.
$C_7H_{13}N$. Calculated % : C 75.67; H 11.71; N 12.61.

Preparation of cyclopentylformaldehyde. Cyclopentanone was prepared by the method of Thorpe and Kün [16], and was converted into the cyclopentylglycidic ester. For this purpose, 42 g of cyclopentanone, 61 g of ethyl monochloroacetate, and 100 ml of benzene were placed in a three-necked flask fitted with a reflux condenser, a stirrer, and a thermometer, and sodamide was added gradually, with constant stirring, in a freezing mixture at −2°. The temperature gradually rises, but should not exceed 15°. Stirring is continued for 2 hrs., after which the yellowish-brown reaction mixture is poured on ice. The benzene layer is separated from the aqueous layer, which is twice extracted with 100 ml portions of benzene. The combined benzene extracts are washed twice with water, once with 3% acetic acid, again with water, and dried over anhydrous sodium sulfate. The benzene is distilled off, and the residue is fractionally distilled at 20 mm pressure, collecting the fraction distilling over at 119-122°; the yield is 29.1 g of practically pure glycidic ester, i.e., about 33.7% of theoretical.

The ester is very readily hydrolyzed by warming its alcoholic solution with sodium ethoxide. The sodium salt so obtained is converted into cyclopentylformaldehyde by the same method as for hexahydrobenzaldehyde, by heating with sulfuric acid in a stream of steam, collecting the aldehyde distilling off in ice-water. The distillate is extracted with ether, the ethereal extract is dried with anhydrous sodium sulfate, and the ether is distilled off. The residue is fractionally distilled under reduced pressure, collecting the fraction boiling at 40-43°/17 mm, which was fairly pure aldehyde; yield 40% of theoretical for the amount of sodium salt taken.

Preparation of β-amino-β-cyclohexylpropionic acid. A mixture of 34.9 g of crystalline aldimine, 28.3 g of malonic acid, 28 ml of 7% ammonia, and 140 ml of alcohol was heated for 8 hrs on a water bath, in a flask connected with a condenser, until evolution of carbon dioxide ceased. Complete dissolution of the substrates does not take place; the white mass gradually shrinks, and turns yellow at the edges, as the alcohol distills off. After completion of the reaction the product is extracted a few times with hot water, when most of it goes into solution, leaving a viscous yellow oil at the bottom of the flask. The aqueous extract is separated, made acid with acetic acid, and extracted with ether, and the ethereal extracts are added to the oil. The solution, thus separated from unreacted aldehyde and from unsaturated acid, is evaporated down until a crystalline crust appears on the surface. The crystalline deposit forming after long standing at low temperature is collected, washed with cold water, in which it is very sparingly soluble, and dried, to give 25.4 g of crystalline product, m.p. 215-216°. Evaporation of the mother liquor gives a further 10.25 g., melting at 211-212°.

The total yield is 35.65 g., or 66% of theoretical calculated on aldimine taken. β-Amino-β-cyclohexyl-propionic acid is readily soluble in alkalis, alcohol, or hot water, difficultly soluble in cold water, and insoluble in ether. After recrystallization from alcohol it melts at 217-218°.

<pre>
         Found   %: C 62.93; 62.74; H 9.83; 9.83; N 8.40; 8.37.
C9H17O2N. Calculated %: C 63.15;   H 9.93;   N 8.18
</pre>

Isolation of cyclohexylacrylic acid. The ethereal extract obtained in the preceding experiment is washed with aqueous bisulfate, to remove traces of aldehyde, and then with water, and is dried over anhydrous sodium sulfate. The ether is distilled off, leaving a yellow, viscous oil with a pungent odor like that of the lower fatty acids. The oil is readily soluble in light petroleum, alcohol, ether and alkalis, but only sparingly soluble in hot water; it may be purified by steam distillation. It crystallizes after long standing in a desiccator containing calcium chloride. The crystals, m.p. 51-53°, are vacuum distilled, to give a colorless, rapidly crystallizing oil, b.p. 153-155°/10 mm., m.p. 56-57°, not changed by recrystallization from alcohol; yield 4.7 g; i.e., about 11% of theoretical, calculated on aldimine taken.

<pre>
         Found   %: C 69.69; 69.70; H 9.15; 9.20.
C9H14O2. Calculated %: C 70.10;   H 9.10.
</pre>

Preparation of β-benzamido-β-cyclohexylpropionic acid. A solution of 10 g of β-amino-β-cyclohexylpropionic acid in 92 ml of 10% sodium hydroxide is treated with constant stirring with 8.2 g of benzoyl chloride added gradually from a dropping funnel. Stirring is continued for another 3 hours, after which the solution is made strongly acid to Congo red with hydrochloric acid. The oil which separates very quickly crystallizes, giving a product which is practically insoluble in cold water, and sparingly soluble in hot water, alcohol, or ether. It is freed of benzoic acid by extracting twice with boiling water, and filtering the hot suspension. The filtrate deposits a small amount of a mixture of benzoic acid and N-benzoyl derivative, m.p. 130-131°. The residue after removal of benzoic acid was dried at 120°, when it melted sharply at 193.5-194°; yield 13.5 g, or 84.5% of theory. The melting point rises to a maximum value of 197-198° after two recrystallizations from alcohol.

$C_{16}H_{21}O_3N$.

Found %: N 5.24; 5.10
Calculated %: N 5.09

Preparation of β-benzamido-β-cyclohexylpropionamide.

A solution of 11.8 g of β-benzamido-β-cyclohexylpropionic acid in 16.9 g of thionyl chloride in a flask fitted with a reflux condenser is heated at 40° until evolution of gas ceases; the reaction is usually completed within $1\frac{1}{4}$ to 2 hours. The excess of thionyl chloride (three times the theoretical amount) is distilled off under reduced pressure (about 12 mm). The acid chloride crystallizing out is dissolved in 600 ml of ether, to give a bright yellow solution, which is saturated for two hours with dry ammonia, with cooling. The precipitate forming is collected, washed with 5% sodium hydroxide solution and then with water, and then recrystallized from alcohol; the yield of pure amide, m.p. 252-253°, was 5.5 g, or 47% of theoretical.

The ethereal mother liquor is decolorized by boiling with active charcoal, the solution is filtered, and the ether is distilled off, leaving 0.77 g of substance of m.p. 160.5-162°, rising to 165-165.5° after recrystallization from alcohol. The substance crystallizes in long, thin needles, which are readily soluble in ether or hot alcohol, but not in water, dilute acids, or alkalis.

The reactions and properties of the substance are identical with those of the tetrahydropyrimidine derivative 4-oxo-2-phenyl-6-cyclohexyltetrahydropyrimidine.

$$
\begin{array}{c}
N = C \cdot C_6H_5 \\
C_6H_{11}CH \quad NH \\
CH_2 - CO
\end{array}
$$
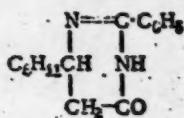
Zvorykina [5], working in our laboratory on the synthesis of compounds of this sort, usually prepared them by heating the benzoyl derivatives with thionyl chloride at 70-80°, whereas in our case the reaction was conducted at 40-45°. The fact that it proceeds under such mild conditions is evidence of the strong tendency of cyclohexyl-amino acid derivatives towards ring-closure. The elementary analysis of the compound obtained by us also confirms the correctness of our supposition.

Found %: C 74.64; 74.83; H 7.93; 8.0; N 10.66; 10.84
$C_{16}H_{20}ON_2$. Calculated %: C 75.00; H 7.81; N 10.93.

Preparation of β-carbomethoxyamino-β-cyclohexylpropionic acid.

Twelve g of methyl chloroformate is added gradually, during an hour, to a cooled solution (0-2°) of 20 g of amino acid in 190 ml of 10% sodium hydroxide, with constant stirring, which is continued for a further 3 hours, after which hydrochloric acid is added to a distinctly acid reaction to Congo red. An oily deposit forms, which soon crystallizes, and which is collected after 10-12 hours, washed with water, and dried at 90°. The carbomethoxy derivative so obtained is fairly pure, m.p. 143-145°, raised to 145.5-146.5° by one recrystallization from alcohol; yield 22 g, or 82% of theoretical.

Found %: N 6.35; 6.20.
$C_{11}H_{19}O_4N$. Calculated %: N 6.11.

Preparation of the amide.

A mixture of 7.9 g of β-carbomethoxyamino-β-cyclohexylpropionic acid and 11.8 g of thionyl chloride is heated at 40° for 3 hrs., until evolution of gas practically ceases, when excess of thionyl chloride is distilled off under reduced pressure. The residual crystalline substance is suspended in ether, in which it is practically insoluble, and the suspension is saturated with ammonia, giving a voluminous precipitate of amide, which is collected after 10-12 hours, washed with 5% sodium hydroxide solution and with water, and dried at 100°. The product melts at 170-175°, and after recrystallization it has m.p. 192-193°, yield 6.5 g, or 82.3% of theoretical. It is sparingly soluble in cold, and readily soluble in hot alcohol.

Found : N 12.44; 12.29.
$C_{11}H_{20}O_3N_2$. Calculated : N 12.28.

Preparation of β-acetamido-β-cyclohexylpropionic acid.

Ten g of acetic anhydride is added gradually, with constant stirring, to 10 g of amino acid in 93 g of 12% aqueous potassium hydroxide at 2-3°, stirring is continued for a further 2 hrs, and hydrochloric acid is added until the solution is distinctly acid to Congo red. It is then evaporated down, and placed in a cool room. The crystalline product which separates after long standing is collected, washed with cold water, and dried; yield 6.5 g, m.p. 159-160°.

Recrystallization from water gives long flat prisms, m.p. 164.5-165.5°. The mother liquor is evaporated to dryness, the residue is extracted with a small amount of dilute alkali, the extract is filtered, and the filtrate is made acid with hydrochloric acid, giving a further 1.1 g of acetyl derivative, m.p. 160.5-161.5°. The total yield is 7.6 g, or 61% of theory.

<div align="center">

Found %: N 6.62; 6.54.

$C_{11}H_{19}O_3N$. Calculated %: N 6.57.

</div>

β-Acetamido-β-cyclohexylpropionamide. 5.9 g of acetyl derivative and 11.5 g of thionyl chloride are heated at 40° in a flask fitted with a reflux condenser. After 2 hrs, during which the substance partly dissolves, and gas is evolved, the excess of thionyl chloride is distilled off, and the crystalline residue of acid chloride is suspended in ether, in which it is practically insoluble. The suspension is saturated with dry ammonia, with vigorous shaking and thorough cooling, and the resulting amide is collected, washed with 5% aqueous sodium hydroxide and then with water, and recrystallized from alcohol; bundles of small needles, m.p. 228-229°, yield 1.9 g, or 32% of theoretical.

<div align="center">

Found % : N 13.0; 12.95.

$C_{11}H_{20}O_2N_2$. Calculated % : N 13.2.

</div>

Hoffmann reaction with β-benzamido-β-cyclohexylpropionamide. A solution of hypobromite prepared from 9.4 g of bromine and 110 g of 15% aqueous potassium hydroxide is cooled to 10°, 7 g of β-benzamido-β-cyclohexylpropionamide is added, and the mixture is stirred at -2 to 0° for 3 hrs. Complete dissolution of the amide does not take place, and the solution still remains turbid after gentle heating on the water bath to 45°, at which temperature the suspended matter coagulates. The flask is then removed from the water bath, but its temperature rises without further heating from 48° to 65°. It is then quickly cooled, when a precipitate separates, which is collected, washed with water, and dried, giving 4.57 g of product melting indefinitely at 196-204°. Two recrystallizations from alcohol give four substances:

1) 2.54 g of substance of m.p. 216.5-217.5°; thin needles insoluble in water, ether, benzene, dilute alkalis and mineral acids, soluble in alcohol and acetic acid. The properties of this substance, and its analytical data, show that it is 1-benzoyl-5-cyclohexylglyoxalidone:

<div align="center">

$C_6H_{11}-CH-NCOC_6H_5$

CH_2-NH CO

</div>
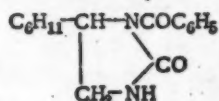
The substance was obtained in 36% yield. (2.54 g).

<div align="center">

Found %: C 70.77; 70.59; H 7.44; 7.29; N 10.24; 10.30.

$C_{16}H_{20}O_2N_2$. Calculated %: C 70.58;   H 7.39;   N 10.29.

</div>

2) 0.17 g of substance of m.p. 205-206°, after recrystallization from alcohol m.p. 215-215.5°, platelets, soluble in dilute hydrochloric acid (1:1) and in alcohol, insoluble in ether and in alkalis. Analysis of this substance showed that it is 5-cyclohexylglyoxalidone; yield about 4% of theoretical. (0.17 g).

<div align="center">

Found % : C 64.14; 64.21; H 10.18; 10.10; N 16.65; 16.68.

$C_9H_{16}ON_2$. Calculated% : C 64.28;   H 9.52;   N 16.67.

</div>

3) 0.22 g of a substance of m.p. 242-243°, identical with the initial amide, the mixed m.p. with which gives no depression. Yield 3%.

4) 0.63 g of a dark-colored, uncrystallizable oil, which was not further studied, owing to the small amount available.

The alkaline mother liquor was treated with bisulfite, and was made acid with hydrochloric acid. The precipitate forming was collected, washed with water, and recrystallized; it melted at 119-120°, and was identical with benzoic acid (yield 0.36 g). Part of the N-benzoyl-cyclohexylglyoxalidone separating in the reaction (0.74 g) was hydrolyzed by heating on a boiling water bath with 20% aqueous sodium hydroxide.

N-Benzoyl-cyclohexylglyoxalidone is insoluble in alkalis, and is only difficultly wetted by water; at the beginning of the reaction it floats on the surface, and only towards the completion of heating does it sink to the bottom of the flask, as a finely crystalline deposit, which is collected, washed with water, and dried;

yield 0.46 g of substance of m.p. 175-183°, raised to 215-215.5° by one recrystallization from alcohol. It does not depress the m.p. of cyclohexylglyoxalidone.

Under the above conditions only about 70-80% of the substance is hydrolyzed, part of it being recovered unchanged. Ether extraction of the acidified solution gives 0.26 g of benzoic acid (78-79% of theoretical).

The Hoffmann reaction was conducted similarly with acetamidocyclohexylpropionamide, which readily dissolves in alkaline hypobromite. The spontaneous rise in temperature is not so great in this case, not exceeding 32°. The oily product soon crystallizes, giving a substance melting indefinitely at 174-178°. Recrystallization from alcohol gives pure cyclohexylglyoxalidone, m.p. 215-215.5°. No intermediate product of the reaction could be isolated, suggesting that it must be very unstable in alkaline solution.

The yield of cyclohexylglyoxalidone from 1 g of amide was 0.35 g, or 44% of theoretical. Acidification of the alkaline solution, followed by ether extraction, gave 0.1 g of brown oil, which was not further investigated.

Hoffmann reaction with N-carbomethoxyamino-β-cyclohexylpropionamide. 2.76 g of amide is added, with stirring, to a hypobromite solution prepared by adding 5.2 g of bromine to 5 g of potassium hydroxide in 33 g of water. Stirring is continued for $1\frac{1}{2}$ to 2 hrs at $-2°$ to .0°, to complete dissolution of the amide, when the flask is transferred to a water bath at 80°. A sudden rise in temperature is observed at 48° to 60° and a voluminous crystalline precipitate forms; at the same time the yellow color of the solution disappears. The suspension is cooled quickly, filtered, and the precipitate is washed with water, and treated with ether, which dissolves only the oily part of the precipitate leaving the crystalline part, which is washed with water and dried; yield of product melting at 153-155° 0.31 g. After washing with hydrochloric acid and recrystallizing from alcohol the m.p. rises to 159.5-160.5°. Analysis of this product shows that it is N-carbomethoxycyclohexylglyoxalidone.

Found % : C 58.94; 59.01; H 7.53; 7.69; N 12.57; 12.63.
$C_{11}H_{16}O_3N$. Calculated % : C 58.40; H 7.96; N 12.39.

The ethereal solution is washed with 1:1 hydrochloric acid, and the ether is then distilled off, to give 0.45 g of an oily residue, which crystallizes on standing in a desiccator. The crystalline product is dissolved in ether, the solution is washed with aqueous alkali, and the ether is distilled off, leaving 0.38 g of a crystalline residue of m.p. 158-160°, not depressing the m.p. of pure carbomethoxycyclohexylglyoxalidone, the total yield of which was thus 0.69 g, or 28% of theoretical.

The dilute hydrochloric acid used for washing the ethereal solution is made alkaline with caustic potash, when 0.13 g of cyclohexylglyoxalidone (6.5% of theoretical) is obtained. Increasing the concentration of alkali leads to reduction in the yield of acylated glyoxalidone. Thus with double the amount of potassium hydroxide the yield of carboxymethyl derivative falls to 4%, and of cyclohexylglyoxalidone rises to 53%.

Preparation of β-ureido-β-cyclohexylpropionic acid. A mixture of 2 g of amino acid and 1.5 g of potassium cyanate in 40 ml of water is heated for 4 hrs on a briskly boiling water bath. After completion of the reaction the solution is cooled, and hydrochloric acid is added to a distinctly acid reaction to Congo red. The gelatinous precipitate is collected and recrystallized from aqueous alcohol; yield 0.75 g (30%) of rosettes of crystals of ureidocyclohexylpropionic acid, m.p. 165-166° (with decomposition)

Found % : N 13.29; 13.14.
$C_{10}H_{16}O_3N_2$. Calculated % : N 13.09.

Preparation of 6-cyclohexyldihydrouracil. 0.3 g of ureido-acid is boiled for 30 min with 100 ml of hydrochloric acid (d 1.12), and the clear solution is evaporated down to small volume. The crystalline precipitate forming from the cooled solution is collected, washed with a small amount of water, and recrystallized from alcohol, to give 0.1 g of cyclohexyldihydrouracil, m.p. 225-226°; yield 36.5%.

Found % : N 14.15; 14.28
$C_{10}H_{16}O_2N_2$. Calculated % : N 14.28

SUMMARY

1. Rodionov's method for synthesis of β-amino acids has been extended to aldehydes of the alicyclic series.

2. A simple method of preparation of hexahydrobenzaldehyde or cyclopentylformaldehyde from cyclohexyl-

or cyclopentyl- glycidic ester, respectively, is described.

3. Condensation of hexahydrobenzaldehyde with malonic acid leads to formation of β-amino-β-cyclohexylpropionic acid, in 50% yield.

4. The yield of β-amino acid is raised to 66% when the aldimine is taken for the condensation instead of the free aldehyde.

5. The N-benzoyl-, N-acetyl-, and N-carbomethoxy- derivatives of β-amino-β-cyclohexylpropionic acid and its amide are described, as well as β-ureodi-β-cyclohexylpropionic acid and cyclohexyldihydrouracil.

6. The Hoffmann reaction is carried out with the acylated derivatives of the aminopropionamides, and it is shown that the N-benzoyl- and N-carbomethoxy- derivatives give 5-cyclohexylglyoxalidone and its N-benzoyl- or N-carbomethoxy- derivatives.

β-Acetamido-β-cyclohexylpropionamide gives only cyclohexylglyoxalidone when treated with hypobromite.

7. The formation of acylated cyclohexylglyoxalidones confirms the correctness of the mechanism proposed by Rodionov and Zvorykina [4] for the Hoffmann reaction of β-amino acids.

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SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO THE STEROIDS. XI

RESEARCHES ON THE STEREOCHEMISTRY OF CYCLIC COMPOUNDS. I. CONDENSATION OF DIVINYL WITH CITRACONIC AND MESACONIC ACID AND THEIR ESTERS. CIS-TRANS-ISOMERISM OF 1-METHYLCYCLO-HEXANE-1,2-DICARBOXYLIC ACIDS AND THEIR ESTERS

I. N. Nazarov and V. F. Kucherov

One of the possible ways of building up polycyclic systems related to the steroids may be through the synthesis of cyclic-trans-dicarboxylic acids (I), with subsequent building up of a side-chain to give the corresponding cyclic derivative of propionic acid (II), which then undergoes ring closure, as follows:
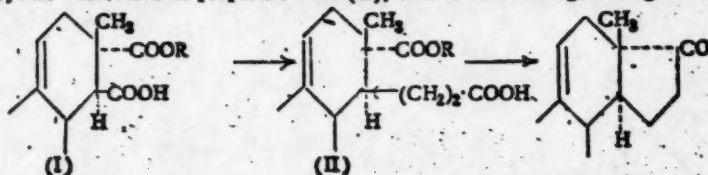
This method was successfully applied by Bachmann [1] for the simplest case of synthesis of cis- and trans-8-methylhydrindan-1-one.

However, the methods given in the literature for synthesizing even the simplest cis- and trans-1-methyl-cyclohexane-1,2-dicarboxylic acids do not give adequate yields of pure product [2]. Even more difficult to prepare are cis- and trans-1-methylcyclohexane-1-carboxy-2-acetic acid [3] or -2-propionic acid [4]. It was for this reason necessary first of all to work out new, more convenient methods of synthesis of compounds of this sort.

It appeared to us that the problem might be solved by the application of methods of diene synthesis, starting with the appropriate transdienophils such as mesaconic acid and its esters. In spite of the great number of papers published on the diene synthesis, we know of only a few examples of the use of trans-dienophils in reactions of diene condensation.

The condensation of fumaric and mesaconic acids with anthracene [5], 1-vinylnaphthalene and 6-methoxy-vinylnaphthalene [6], of fumaryl chloride with divinyl [7] and of fumaric acid with piperylene [8], and certain other cases have been described in the literature.

We began this work on the systematic study of diene condensations with trans-dienophils with the simplest cases, taking divinyl as the diene component, and studying its condensation with citraconic anhydride and citraconic or mesaconic acids and their esters.

One mol of citraconic anhydride (III) is heated for 4 hrs at 130° with 3 mol of divinyl, to give the anhydride (V) of cis-1-methyl-cyclohex-4-ene-1,2-dicarboxylic acid, in 85% yield, calculated on actually reacted citraconic anhydride; this substance has already been described [9, 10]. It is hydrolyzed by boiling water, giving cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (VI), m.p. 168° (also previously described), which when hydrogenated with Pd catalyst affords cis-1-methylcyclohexane-1,2-dicarboxylic acid (VII), which has also been described before, and which when cautiously heated with acetyl chloride yields the corresponding anhydride (VIII), m.p. 72°, also prepared by hydrogenation of the unsaturated anhydride (V) with Pd catalyst in dioxan.

The same anhydride (V) is obtained in 70% yield by heating citraconic acid (IV) with 3 mol of divinyl at 110° for 4 hrs. Mesaconic acid (IX) condenses with divinyl with much more difficulty than does citraconic acid and its anhydride. Thus when 1 mol of mesaconic acid is condensed with 8 mol of divinyl in dioxan (3 hrs at 170°) the yield of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X), m.p. 180°, amounts to 40%; 40% of the mesaconic acid taken remains unchanged in the reaction mixture, and product (X) has to be separated from it by fractional crystallization.

(III)   (IV)

(V)   130°   110°

(IX)   240°   170°   (X)   KOH

(XIV)   210°   (XV)

CH₃ONa   210°   (VI)   (XVII)
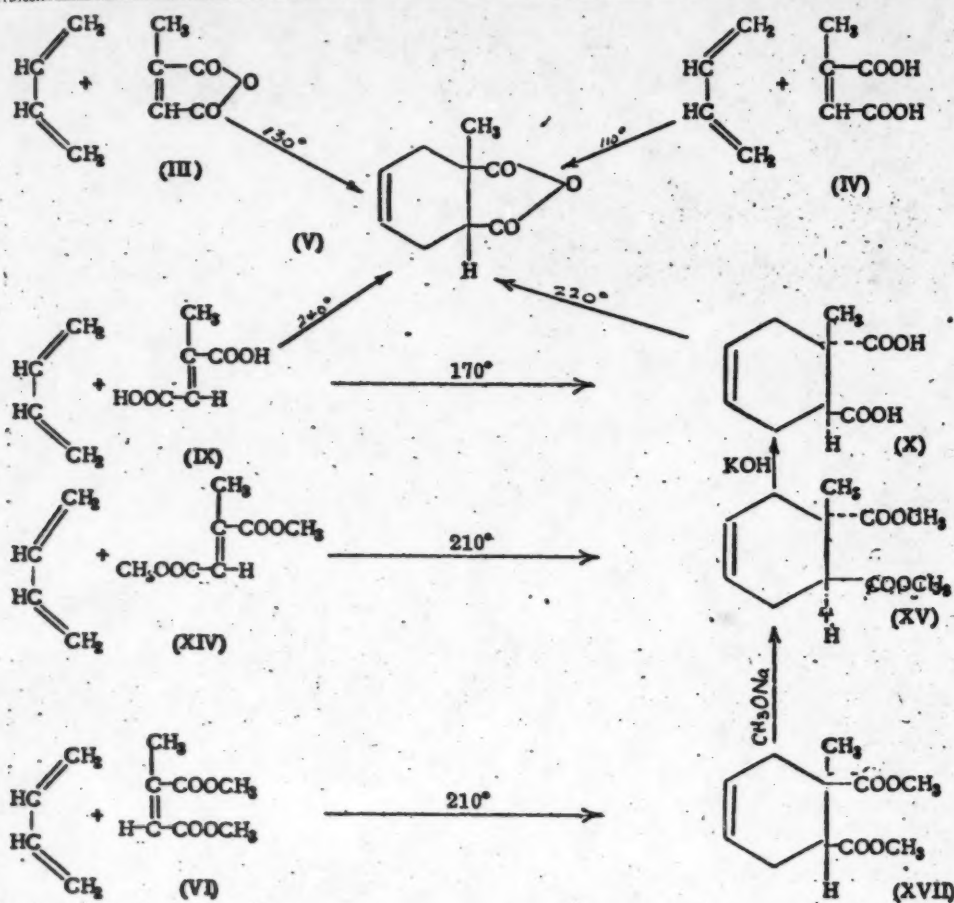
Hydrogenation of the trans-acid (X) in methanol solution with Pd catalyst gives trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI), m.p. 213-214°, which has been described in the literature [1,2,11]; trans-1-methylcyclo-hex-4-ene-1,2-dicarboxylic acid (X) and acetyl chloride give the corresponding unsaturated trans-anhydride (XII), m.p. 79°, hydrogenation of which (Pd catalyst) affords the anhydride of trans-1-methylcyclohexane-1,2-dicarboxylic acid (XIII), m.p. 87°, also obtained from the trans-acid (XI) by the action of acetyl chloride. The anhydrides (XII) and (XIII) are readily hydrolyzed by boiling water, giving the pure trans-acids (X) and (XI), respectively, and are converted into the corresponding cis-acids (VI) and (VII) when heated with dioxan at 200-220°, followed by hydrolysis.

Condensation of mesaconic acid with divinyl did not take place under milder conditions (3 hr. at 110°). The chief product under more drastic conditions (4 hr. at 220-240°) is the anhydride of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (V), obtained in up to 50% yield. This thermal isomerization of trans- to cis-isomer established for the cases of the trans-anhydrides (XII) and (XIII) was also found for pure trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X), which is largely converted into the cis-isomer (VI) by heating for 3 hr. in dioxan at 200°.

(X)   →   (VI)
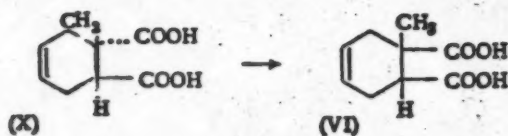
These findings confirm earlier observations of the greater stability of the cis-configuration of 1-methylcyclohexane-1,2-dicarboxylic acid, as compared with the corresponding non-methylated dicarboxylic acid. As has been noted by Linstead [2], cis-1-methylcyclohexane-1,2-dicarboxylic acid when treated with concentrated hydrochloric acid at 180° gives a mixture containing only about 15% of the trans-isomer, whereas cis-hexahydrophthalic acid is

H₂(Pd) labels...

(V) $\xrightarrow{\text{H}_2(\text{Pd})}$ (VIII) m.p. 72°

Dioxan

(VI) m.p. 168° $\xrightarrow{\text{H}_2(\text{Pd})}$ (VII) m.p. 158°

Methanol

(XII) m.p. 79° $\xrightarrow{\text{H}_2(\text{Pd})}$ (XIII) m.p. 87°

Dioxan

(X) m.p. 180° $\xrightarrow{\text{H}_2(\text{Pd})}$ (XI) m.p. 213°

Methanol
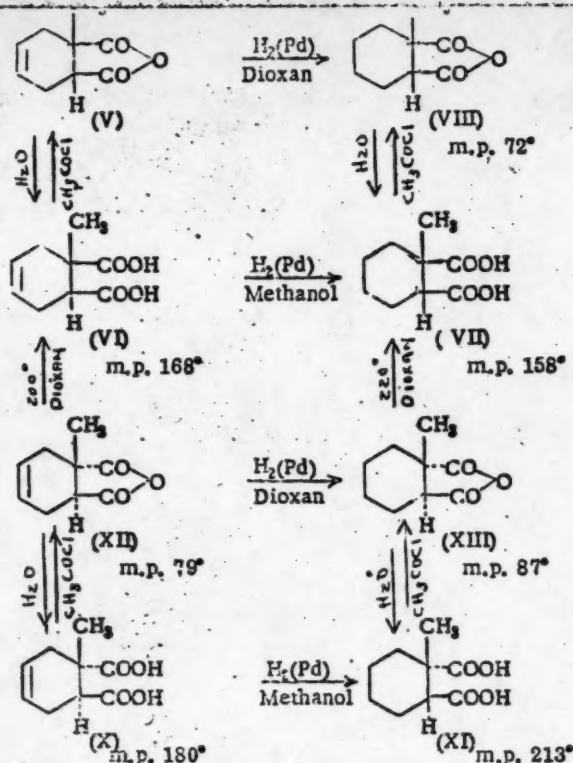
quantitatively converted into the trans-isomer under these conditions. We have shown that cis- (VII) and trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI) give the same equilibrium mixture, containing about 80% of cis- and 20% of trans-isomer, when heated with concentrated hydrochloric acid at 180°, suggesting the equilibrium:

(VII) 80% $\xrightarrow{\text{HCl, 180°}}$ (XI) 20%
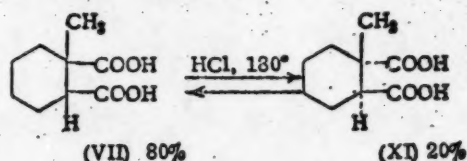
Dimethyl mesaconate (XIV) condenses fairly readily with divinyl. When 1 mol. of the ester (XIV) is heated for 3 hours at 210° with 5 mol. of divinyl in benzene a yield of up to 90% of the reacted ester is obtained as dimethyl trans-1-methylcyclohex-4-ene-1,2-dicarboxylate (XV), b.p. 97°/2 mm., n_D^{20} 1.4740. When hydrolyzed with 20% aqueous potassium hydroxide it gives trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X), and when hydrogenated (Pd catalyst in methanol) it affords dimethyl trans-1-methyl-cyclohexane-1,2-dicarboxylate (XVI), which when hydrolyzed with 20% caustic potash gives pure trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI). The structure of the dimethyl esters (XV) and (XVI) was established by synthesizing them from the corresponding trans-acids (X) and (XI), which were methylated with diazomethane in ethereal solution.

Dimethyl citraconate does not react readily with divinyl. The reaction hardly proceeds at all at 170°, while under similar conditions as for dimethyl mesaconate (4 hr. at 210°) the product contains only 12% of condensate, the rest being unchanged ester. Hydrolysis of the condensate with 20% caustic potash gives cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (VI) (overall yield not more than 10%). These observations are in line with the earlier one that divinyl reacts with cis-cinnamic acid much less readily than with trans-cinnamic acid [12].

Pure dimethyl cis-1-methylcyclohex-4-ene-1,2-dicarboxylate (XVII), b.p. 98°/2 mm., n_D^{20} 1.4745, was obtained from the cis-acid (VI) by methylation with diazomethane, and was hydrogenated (Pd catalyst), to afford dimethyl cis-1-methylcyclohexane-1,2-dicarboxylate (XVIII), also prepared by methylation of the cis-acid (VII) with diazomethane. (See top of next page for diagram).

Trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X) is obtained in 40% yield by prolonged boiling of dimethyl cis-1-methylcyclohex-4-ene-1,2-dicarboxylate (XVII) with 15% sodium methoxide in methanol, followed by hydrolysis of the product. Under the same conditions dimethyl cis-1-methylcyclohexane-1,2-dicarboxylate (XVIII) gives up to 65% yields of trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI). The degree of isomerization is much smaller under milder conditions.

EXPERIMENTAL

Citraconic acid was prepared in the usual way by the pyrolysis of citric acid [13]. Mesaconic acid was obtained by isomerization of citraconic anhydride with dilute nitric acid [14]. Dimethyl citraconate and mesaconate were prepared by esterification of the appropriate acids in the presence of sulfuric acid [15].

I. Condensation of divinyl with citraconic anhydride.

A solution of 17 g of citraconic anhydride (b.p. 103-106°/20 mm, n_D^{20} 1.4720) and 25 g of divinyl in 150 ml of dry benzene is heated in a steel cylinder for 4 hours at 130-135°. The benzene solution is separated from the solid

CH₃ structures on left side:

CH_3 —COOCH₃ —COOCH₃ H (XV) $\xrightarrow{H_2(Pd)}$ CH_3 —COOCH₃ —COOCH₃ H (XVI)

CH_3 —COOH —COOH H (X) $\xrightarrow{H_2(Pd)}$ CH_3 —COOH —COOH H (XI)

CH_3 —COOCH₃ —COOCH₃ H (XVII) $\xrightarrow{H_2(Pd)}$ CH —COOCH₃ —COOCH₃ H (XVIII)

CH_3 —COOH —COOH H (VI) $\xrightarrow{H_2(Pd)}$ CH —COOH —COOH H (VII)
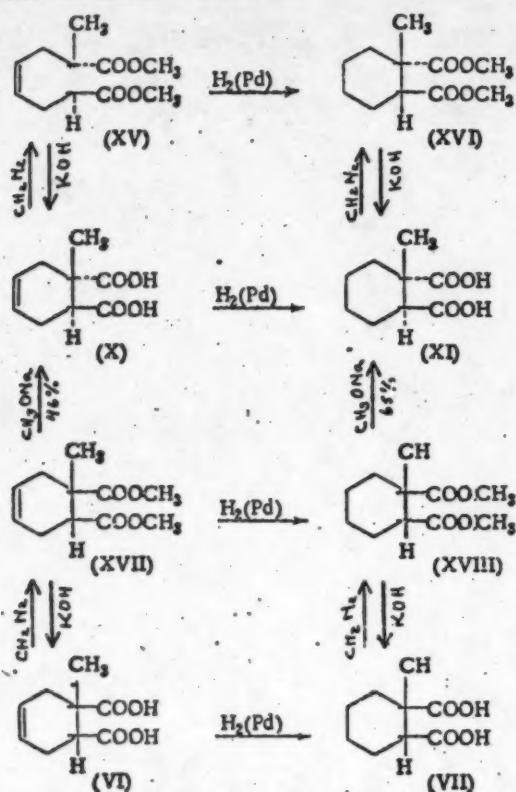
polymer of divinyl which forms, the benzene is distilled off, and the residue is vacuum-distilled, collecting the fraction boiling at 111-115°/4 mm., which is redistilled, to give 18.5 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (V), b.p. 113-115°/4 mm., n_D^{20} 1.4890.

Hydrolysis of the anhydride (V). 3.5 g of anhydride is boiled with 5 ml of water for about 20 min., until it dissolves. The crystalline product separating from the solution is collected. A yield of 3.8 g of acid of m.p. 165-166°, is thus obtained, giving pure cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (VI), m.p. 168°, when recrystallized from water; the m.p. coincides with that cited in the literature [10].

Hydrogenation of the acid (VI). 1.7 g of acid (VI) is hydrogenated in methanol solution in presence of Pd catalyst, 1 mol. of hydrogen being absorbed (210 ml at 0° and 760 mm). The solvent is distilled off, leaving 1.65 g of cis-1-methylcyclohexane-1,2-dicarboxylic acid (VII), which melts at 158° after recrystallization from water. 0.4 g of this acid (VII) is heated in a sealed glass tube with 3 ml of concentrated hydrochloric acid for 7 hours at 180°; the product crystallizing out from the cooled solution melts indefinitely at 145-190°. Fractional crystallization from water and aqueous acetone gives 0.05 g of trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI), m.p. 210-212°.

Cis-1-Methylcyclohexane-1,2-dicarboxylic anhydride (VIII). a) 3 g of the anhydride (V) in 15 ml of absolute dioxan is hydrogenated, over Pd catalyst, 1 mol. of hydrogen being absorbed (420 ml at 17°/750 mm). The solvent is distilled off in vacuum, leaving a liquid product, which, after repeated treatment with light petroleum, distilling off the solvent in vacuum, and cooling the residue, finally crystallizes, giving 2.9 g of a product of m.p. 69-71°, raised to 71-72° by recrystallization from light petroleum.

Found %: C 64.48; 64.63; H 7.45; 7.43. C₉H₁₂O₃. Calculated %: C 64.30; H 7.20.

Hydrolysis of this anhydride (VIII) by boiling with water gives a quantitative yield of cis-1-methylcyclohexane-1,2-dicarboxylic acid (VII), m.p. 157-158°.

b) 0.7 g of cis-1-methylcyclohexane-1,2-dicarboxylic acid (VII) is boiled with 3 ml of acetyl chloride on a water bath, for about 20 min., until it dissolves. The acetyl chloride is distilled off in vacuum, and the residue, which crystallizes after treatment with light petroleum, is recrystallized from light petroleum, giving 0.5 g of cis-anhydride (VIII) of m.p. 72-72.5°.

II. Condensation of Divinyl with Citraconic Acid (IV)

A solution of 6.5 g of citraconic acid (m.p. 91-93°) and 8 g of divinyl in 50 ml of anhydrous benzene, with a small amount of phenyl-2-naphthylamine, is heated for 4 hours at 110-115° in a sealed tube. The benzene solution is separated from the water formed in the reaction, and the benzene is distilled off in vacuum. The residue is a viscous oil, not crystallizing after treatment with various solvents, and after long standing. Vacuum distillation gives 5.5 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic anhydride (V), b.p. 105-107°/2.5 mm, n_D^{20} 1.4885.

III. Condensation of Divinyl with Mesaconic Acid (IX)

a) A solution of 6.5 g of mesaconic acid (m.p. 203-205°) and 25 g of divinyl in 150 ml of dioxan is heated for 3 hours at 170-175° in a steel cylinder. The solvent is then distilled off in vacuum, the residue is treated with dry benzene, and the crystalline product is collected by filtration, giving 7.25 g of substance of m.p. 135-160°, which when :: recrystallized from acetone affords 4.9 g of product of m.p. 155-170°, from which a second recrystallization from acetone with a little light petroleum gives a pure product (2.1 g), of m.p. 180-182°. The residual solutes

in the mother liquors are twice recrystallized from water, giving 1.7 g of substance of m.p. 160-175°, which is re-crystallized from 10:1 acetone-petroleum ether mixture, giving a further 0.85 g of product of m.p. 179-181°. The total yield of condensation product is 2.95 g (35.5%) of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X), m.p. 180-181°.

Found %: C 59.04; 58.91; H 6.89; 7.15. $C_9H_{12}O_4$. Calculated %: C 58.70; H 6.80.

The crystalline substance (3.8 g) remaining after separation of the acid (X) is chiefly unchanged mesaconic acid with a small admixture of the acid (X); it may be used for further condensation.

b) A mixture of 1.3 g of mesaconic acid, 5.5 g of divinyl, 25 ml of dioxan, and a small amount of phenyl-2-naphthylamine is heated for 4 hours at 240-245° in a sealed tube. The solvent is distilled off, leaving a dark-colored, viscous oil, which is soluble in benzene but does not crystallize from it or from other solvents. Vacuum distillation gives 0.7 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic anhydride (V), b.p. 108-110°/3 mm., n_D^{20} 1.4895, which is hydrolyzed, and the product is recrystallized from water, giving 0.5 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (VI), m.p. 166-168°.

Isomerization of the trans-acid (X). 0.25 g of trans-acid (X) is heated with 3 ml of dioxan for 3 hours at 200-210°, in a sealed tube. The solvent is distilled off, and the oily residue is hydrolyzed, giving 0.2 g of crystalline product, m.p. 135-150°, recrystallization of which from a 5:1 acetone-benzene mixture gives 0.1 g of cis-1-methyl-cyclohex-4-ene-1,2-dicarboxylic acid (VI), m.p. 168-169°, not depressing the melting point of a sample of pure cis-acid (VI).

Hydrogenation of trans-acid (X). 0.5 g of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X) in 10 ml of methanol is exhaustively hydrogenated, using Pd catalyst. The solvent is distilled off in vacuum, leaving 0.48 g of crystalline product, m.p. 208-210°, recrystallization of which from 40% aqueous acetone gives 0.35 g of trans-1-methyl-cyclohexane-1,2-dicarboxylic acid (XI), m.p. 212-213°, in agreement with published data [2, 11]. This acid does not depress the m.p. of a sample of trans-acid (XI) obtained by isomerization of the cis-acid (VII) with concentrated hydrochloric acid.

Found %: C 57.80; 57.70; H 7.64; 7.68. $C_9H_{14}O_4$. Calculated %: C 58.0; H 7.60.

Isomerization of the trans-acid (XI). 0.3 g of trans-acid (XI) is heated with 3 ml of concentrated hydrochloric acid for 7 hours at 190°, in a sealed tube. Fractional crystallization from water and aqueous acetone of the crystalline product obtained gave 0.03 g of the initial trans-acid (XI) and 0.1 g of cis-acid (VII), m.p. 156-158°.

Anhydride of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (XII). One g of trans-acid (X) is heated on a water bath with boiling acetyl chloride until it passes completely into solution (20 min.), when the excess of acetyl chloride is distilled off in vacuum. The residual oil gradually crystallizes, and after recrystallization from light petroleum gives 0.8 g of trans-anhydride (XII), m.p. 78-79°.

Found %: C 65.20; 65.31; H 6.19; 6.21. $C_9H_{10}O_3$. Calculated %: C 65.04; H 6.06.

This anhydride is hydrolyzed by boiling with water, giving the initial trans-acid (X) in quantitative yield (m.p. 180-181°).

Isomerization of the trans-anhydride (XII). 0.2 g of trans-anhydride (XII) are heated for 2 hours at 190-200° with 3 ml of dioxan, in a steel cylinder. The liquid residue remaining after distilling off the dioxan is hydrolyzed by boiling with water, and the resulting cis-acid (VI) is twice recrystallized from water, giving 0.08 g of product melting at 165-167°.

Trans-1-Methylcyclohexane-1,2-dicarboxylic anhydride (XIII). a) 0.5 g of trans-acid (XI) and 3 ml of acetyl chloride are heated at the b.p. to complete dissolution, and the acetyl chloride is then distilled off in vacuum. The residual oily product gradually crystallizes when treated with light petroleum, after recrystallization from which 0.35 g of trans-anhydride (XIII), m.p. 87-88°, is obtained.

Found %: C 64.36; 64.43; H 7.29; 7.33. $C_9H_{12}O_3$. Calculated %: C 64.30; H 7.20.

The initial trans-acid (XI), m.p. 212-213°, is obtained quantitatively by hydrolyzing the anhydride (XIII) with water.

b) 0.4 g of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic anhydride (XII) in 5 ml of absolute dioxan is hydro-genated, using Pd catalyst. The liquid residue remaining after distilling off the solvent in vacuum is recrystallized from light petroleum, giving 0.3 g of anhydride (XIII), m.p. 87-88°.

Isomerization of the trans-anhydride.(XIII). 0.3 g of the trans-anhydride (XIII) is heated with 4 ml of dioxan in a sealed tube for 2 hours at 200-210°. The liquid residue remaining after distilling off the dioxan is hydrolyzed by boiling with water, and the product is twice recrystallized from water, giving 0.2 g of pure cis-acid (VII), m.p. 157-158°.

IV. Condensation of divinyl with dimethyl mesaconate (XIV).

A mixture of 9.2 g of dimethyl mesaconate (b.p. 90-91°/12 mm, n_D^{20} 1.4460), 16.5 g of divinyl, and 40 ml of dry benzene is heated for 3 hours at 210-215° in a steel cylinder. The solvent is distilled off, and the residue is fractionated in vacuum:

Fraction 1, b.p. 65-95°/3 mm., n_D^{20} 1.4650; weight 2.2 g.
Fraction 2, b.p. 99-102°/3 mm., n_D^{20} 1.4735; weight 8.5 g.

A large amount of divinyl polymer remains in the flask. A second fractional distillation gives 1.8 g of the initial dimethyl mesaconate (n_D^{20} 1.4480) and 8.7 g of dimethyl trans-1-methylcyclohex-4-ene-1,2-dicarboxylate (XV), yield 87% calculated on reacted mesaconic ester, b.p. 97°/2 mm, n_D^{20} 1.4742, d_4^{29} 1.1170; MR_D found 53.41, calculated 53.64.

Found %: C 62.25; 62.19; H 7.62; 7.79. $C_{11}H_{16}O_4$. Calculated %: C 62.50; H 7.60.

The trans-diester (XV) was also obtained from trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X) and diazomethane in ethereal solution; it had the same constants (b.p. 97°/2 mm., n_D^{20} 1.4738).

Hydrolysis of the trans-diester (XV). 3.2 g of trans-diester (XV) is boiled with 20 ml of 20% aqueous caustic potash until it dissolves (about 20 min.). The light yellow solution is filtered through active charcoal, and concentrated hydrochloric acid is added to the filtrate until it becomes acid to Congo red. 2.6 g of acid of m.p. 179-181°, not depressing the m.p. of a sample of pure trans-acid (X), is obtained.

Hydrogenation of trans-ester (XV). 3.2 g of dimethyl trans-1-methyl-cyclohex-4-ene-1,2-dicarboxylate (XV) in 20 ml of methanol is hydrogenated, using Pd catalyst. One mol. of hydrogen was absorbed (335 ml at 0° and 760 mm). The methanol was distilled off, and the residue was fractionally distilled in vacuum, giving 3 g of dimethyl trans-1-methyl-cyclohexane-1,2-dicarboxylate (XVI), b.p. 95°/2 mm., n_D^{20} 1.4639, d_4^{20} 1.0940; MR_D Found 53.95, Calculated 54.11.

Found %: C 61.57; 61.39; H 8.60; 8.63. $C_{11}H_{18}O_4$. Calculated %: C 61.60; H 8.45.

The same ester (XVI), b.p. 95°/2 mm., n_D^{20} 1.4636, was obtained in theoretical yield by the action of diazomethane on the trans-acid (XI) in ethereal solution.

The trans-ester (XVI) (0.5 g) is boiled with 5 ml of 20% aqueous caustic potash until it goes into solution, the solution is filtered through active charcoal, the filtrate is made acid to Congo red, and the precipitate forming is collected, and recrystallized from 50% aqueous acetone, giving 0.35 g of trans-1-methylcyclohexane-1,2-dicarboxylic acid (XI), m.p. 211-213°, not depressing the m.p. of a sample of pure trans-acid (XI).

V. Condensation of divinyl with dimethyl citraconate.

A mixture of 9.8 g of dimethyl citraconate (b.p. 96-97°/12 mm; n_D^{20} 1.4470) and 17 g of divinyl in 40 ml of dry benzene is heated in a steel cylinder for 3 hours at 210-215°. The residue after distilling off the solvent is extracted with acetone, in order to separate the product from divinyl polymer, the acetone is distilled off, and the residue is fractionally distilled in vacuum.

Fraction 1, wt. 6.1 g., b.p. 99-109°/15 mm; n_D^{20} 1.4550.
Fraction 2, wt. 2.5 g., b.p. 110-130°/15 mm; n_D^{21} 1.4700.

Redistillation of Fraction 1 gave 5.6 g of pure dimethyl citraconate (b.p. 97°/12 mm; n_D^{20} 1.4490). Repeated fractionation of Fraction 2 gave 1.6 g of condensation product, b.p. 97-100°/2 mm; n_D^{20} 1.4715, hydrolysis of which with 20% aqueous caustic potash gives cis-1-methyl-cyclohex-4-ene-1,2-dicarboxylic acid (VI), m.p. 167-168°, yield after recrystallization 1.2 g., or 10-12% of theoretical.

VI. Preparation of dimethyl cis-1-methylcyclohex-4-ene-1,2-dicarboxylate (XVII), and its isomerization.

A slight excess of diazomethane in ether is added gradually to a suspension of 6 g of cis-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (VI) in 40 ml of absolute ether, the ether is distilled off, and the residue is fractionally distilled in vacuum, giving 6.5 g of dimethyl ester (XVII), b.p. 98°/2 mm; n_D^{20} 1.4745; d_4^{20} 1.1210; MR_D

found 53.28, calculated 53.64.

Found %: C 62.41; 62.26; H 7.64; 7.77. $C_{11}H_{16}O_4$. Calculated %: C 62.50; H 7.60.

Hydrolysis of the dimethyl ester (XVII) with 20% aqueous caustic potash regenerates the initial cis-acid (VI), in theoretical yield.

Isomerization of the cis-ester (XVII). A mixture of 4.5 g of cis-ester (XVII) and sodium methoxide (12 g of sodium dissolved in 300 ml of absolute methanol) in methanol is boiled on a water bath for 12 hours. The methanol is distilled off in vacuum, the residue is dissolved in a small volume of water, the solution is extracted with ether, and the aqueous layer is evaporated down to small volume in a porcelain bowl on a water bath. The deposit of sodium salts forming is filtered off and dissolved in 20 ml of water, 60% sulfuric acid is added to an acid reaction to Congo red, and the crystalline precipitate forming is collected; yield, 2.5 g of acid of m.p. 168-175°, or, after crystallization from 10:1 acetone-light petroleum mixture, 1.8 g (46% of theoretical) of trans-1-methylcyclohex-4-ene-1,2-dicarboxylic acid (X), m.p. 179-181°, not depressing the m.p. of a sample of known pure acid.

VII. Preparation of dimethyl cis-1-methylcyclohexane-1,2-dicarboxylate (XVIII), and its isomerization.

Similarly to the preceding experiment, 4.8 g of cis-1-methylcyclohexane-1,2-dicarboxylic acid (VII) and diazomethane in ether gave 5.1 g of pure cis-ester (XVIII), b.p. 95°/2 mm, n_D^{20} 1.4635, d_4^{20} 1.0935; MR_D found 54.01, calculated 54.11.

Found %: C 61.35; 61.25; H 8.48; 8.37. $C_{11}H_{18}O_4$. Calculated %: C 61.60; H 8.45.

The dimethyl ester (XVIII) is also obtained in theoretical yield by hydrogenation of dimethyl cis-1-methyl-cyclohex-4-ene-1,2-dicarboxylate (XVII) in methanol solution, using Pd catalyst. Hydrolysis of the ester with 20% aqueous caustic potash gives the cis-acid (VII) in theoretical yield.

Isomerization of the cis-ester (XVIII). 4.1 g of cis-ester (XVIII) is boiled for 12 hours on a water bath with a solution of sodium methoxide prepared from 10 g of sodium and 250 ml of absolute methanol. The solution is evaporated to dryness in vacuum, the residue is dissolved in a small volume of water, and the solution is extracted with ether. The aqueous solution is evaporated down to small volume in a porcelain basin on a water bath, the deposit of sodium salts is collected, and dissolved in 15 ml of water, which is filtered through active charcoal, and the filtrate is made acid to Congo red with concentrated hydrochloric acid, giving 2.75 g of acid of m.p. 197-205°, which when recyrstallized from 60% aqueous acetone gives 2.3 g (65% of theoretical) of pure trans-1-methyl-cyclohexane-1,2-dicarboxylic acid (XI), m.p. 212-213°, not depressing the m.p. of a known sample of the acid.

SUMMARY

1. Condensation of divinyl with citraconic anhydride, citraconic acid, mesaconic acid, and their dimethyl esters gives the cis- and trans-1-methyl-cyclohexane-1,2-dicarboxylic acids (VI), (VII), (X), and (XI), their anhydrides (V), (VIII), (XII), and (XIII), and their dimethyl esters (XV), (XVI), (XVII), and (XVIII).

2. Condensation of divinyl with dimethyl mesaconate gives dimethyl trans-1-methylcyclohex-4-ene-1,2-dicarboxylate (XV) in good yield; the trans-acids (X), and (XI) are readily hence derived.

3. The dimethyl esters of the cis-acids (XVII) and (XVIII) are converted by the action of sodium methoxide into the corresponding trans-acids (X) and (XI), in good yield.

4. The trans-acids (X) and (XI), and their anhydrides (XII) and (XIII) isomerize when heated at 200°, to afford the corresponding cis-compounds.

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• See Consultants Bureau translation, p. 2079.

SYNTHESIS OF STEROID COMPOUNDS AND OF RELATED SUBSTANCES. XII. CONDENSATION OF CYCLIC β-DIKETONES WITH VINYL KETONES, AND TRANSFORMATIONS OF THE RESULTING PRODUCTS

I. N. Nazarov and S. I. Zavyalov

Methoxy-octalone (I), prepared in our laboratory by the condensation of 2-methoxybutadiene with 1-methyl-cyclohex-1-ene [1], is an important intermediate for the synthesis of steroid compounds:
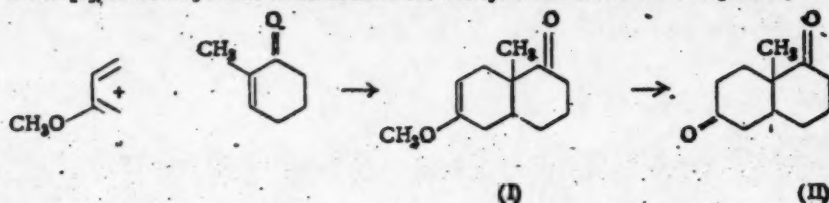
Hydrolysis of methoxyoctalone (I) with dilute acids gives diketomethyldecalin (II). Since the above ketones (I) and (II) were obtained by the method of diene condensation they must belong to the cis-decalin series, so that they can be used for the synthesis of only such steroid systems as have the cis-configuration of rings A and B. However, most of the biologically important steroids, in particular the steroid hormones, have the A-B and C-D rings joined in the trans-position. Many important steroid hormones (progesterone, testosterone, corticosterone, cortisone, etc.) have a double bond at C_4-C_5 in the ring system A-B. For these reasons we thought it necessary to work out convenient methods for the preparation of 1,6-diketo-9-methyl-Δ^5-octalin (VI), as a starting substance for the synthesis of these steroid hormones and of other related substances.

With this end in view we decided to begin our studies with the reaction of condensation of vinyl ketones with methyldihydroresorcinol, with cyclization of the resulting product, according to the scheme:
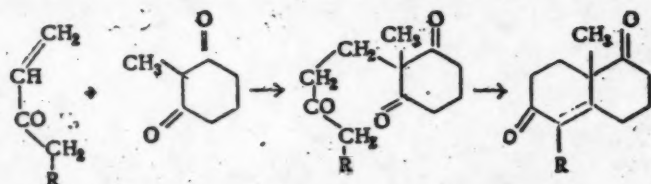
Methyldihydroresorcinol (IV) condenses with vinyl methyl ketone (III) in the presence of sodium methoxide in methanol, to give the triketone (V) in 60-65% yield, together with a small amount of the cyclic ketoacid (VIII), formed as a result of hydrolytic fission of the triketone (V), followed by cyclization of the diketo-acid (VII), arising as an intermediate product.
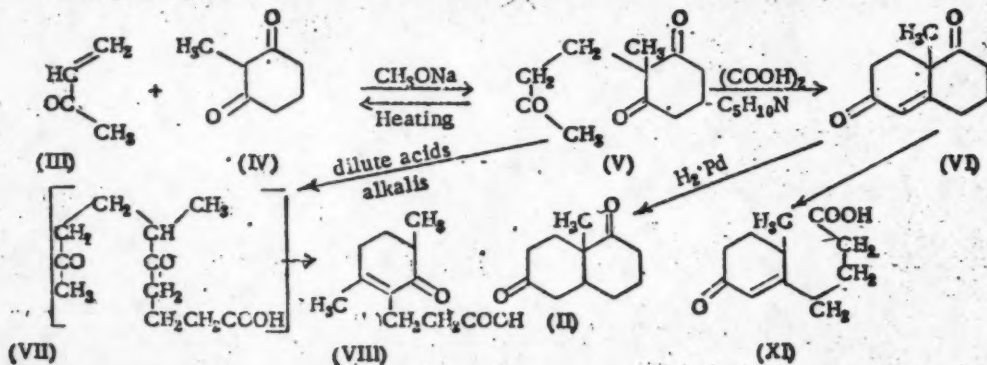
The triketone (V) was in fact found to be very readily hydrolyzable, both by dilute acids and alkalis at room temperature, with opening of the dihydroresorcinol cycle, giving the intermediate product (VII), which undergoes ring closure with production of the unsaturated keto-acid (VIII), the structure of which was established from a study of its ozonation products, viz., succinic acid (IX) and hexan-5-one-2-carboxylic acid (X):
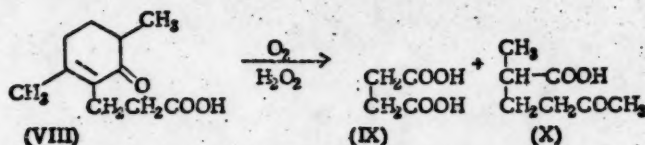
The latter acid was also synthesized from acetoacetic and methacrylic esters, which were condensed, the product was hydrolyzed, and the hexan-2-one-3,5-dicarboxylic acid so obtained was decarboxylated, giving hexan-5-one-2-carboxylic acid [2]:

The triketone (V) decomposes when distilled in vacuum (15-20 mm), giving methyldihydroresorcinol. When heated with phosphorus pentoxide it affords chromanone (XII) in high yield:

The extraordinary ease of hydrolysis of the triketone (V), with its conversion into the keto-acid (VIII), was the chief obstacle in realizing cyclization of triketone (V) into diket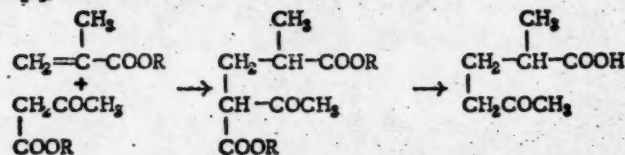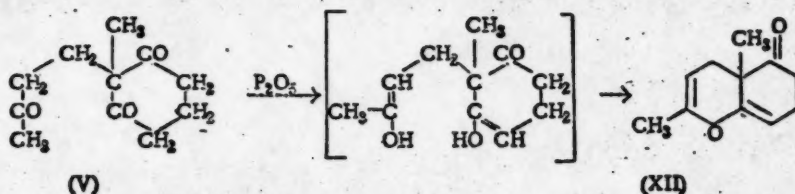o-octalin (VI). This important reaction was studied in the greatest detail, the best results being obtained when the triketone (V) was heated with salts of secondary amines, when the yield of diketo-octalin (VI) was 60% or more. The yield was much lower when the triketone (V) was heated with piperidine in benzene solution, or with anhydrous oxalic acid in vacuo. Diketo-octalin (VI) itself readily undergoes hydrolytic decomposition with dilute alkalies, giving in all probability, the unsaturated keto-acid (VIII) or other isomeric acids. •

The bicyclic diketone (VI) was recently prepared, in very small yield, by Wieland and Miescher [3], from methyldihydroresorcinol and 1-diethylaminobutan-3-one methiodide:
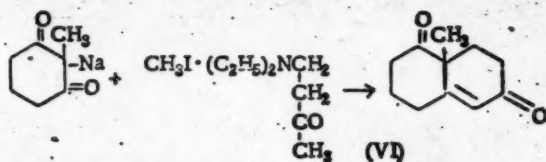
The Swiss chemists did not, however, establish the structure of the product obtained by them. We were able to do this by showing that the hydrogenation product is identical with cis-1,6-diketo-9-methyldecalin (II), which had previously been prepared in our laboratory.

Methyldihydroresorcinol (IV) also condenses smoothly with 5-carbomethoxypent-1-en-3-one (XIV) in the presence of sodium ethoxide, giving the addition product (XV), where R=CH₃, which was not isolated pure, since it decomposed when distilled, even in a very high vacuum (0.05 mm). For this reason the triketoester (XV, R=CH₃)

* While we were preparing this paper for publication a paper by Tischler et al. appeared, in which certain of the transformations described by us were included; in particular, the product of hydrolysis of octalin (VI) is assigned the structure (XI) [4].

was subjected to cyclization without previous purification, by heating in vacuum with anhydrous oxalic acid, when crystalline 1;6-diketo-5-carboxymethyl-8-methyl-Δ⁵-octalin (XVI) is obtained in good yield.

When heated with hydrochloric acid the triketoester (XV, R = CH₃) changes fairly readily into the unsaturated cyclic keto-dicarboxylic acid (XVIII), by the above-described process of hydrolytic fission of the dihydroresorcinol cycle, with subsequent cyclization of the intermediate product, diketocarboxylic acid (XVII). The reaction of cyclization of the triketoester of dihydroresorcinol (XV, R = CH₃) was found to be reversible, as the diketo-octalin derivative (XVI) is readily converted by heating with hydrochloric acid into the keto-dicarboxylic acid (XVIII), by hydrolytic fission, through the intermediate compounds (XV, R = CH₃) and (XVII). In the same way the diketo-octalin derivative (XVI) is converted in practically quantitative yield into the dimethyl ester (XIX) when treated with a solution of hydrogen chloride in anhydrous methanol.
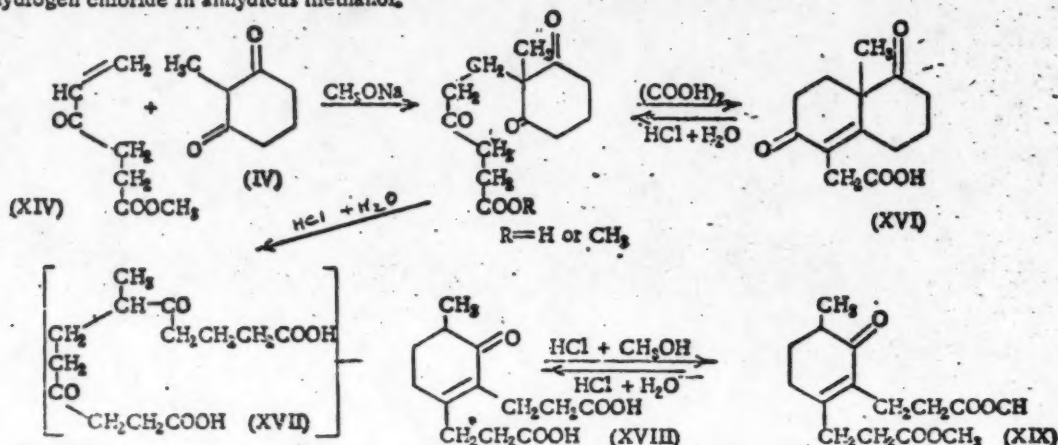
Hydrolysis of the dimethyl ester (XIX) with dilute hydrochloric acid gives the ketodicarboxylic acid (XVIII), the structure of which was established, as in the preceding case, by identification of the ozonation products, succinic acid and heptan-3-one-1,6-dicarboxylic acid (XX):
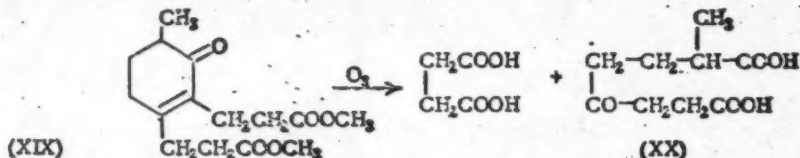
Condensation of but-1-en-3-one with the acid (XXI) in presence of sodium methoxide gives the diketolactone (XXII), in good yield:
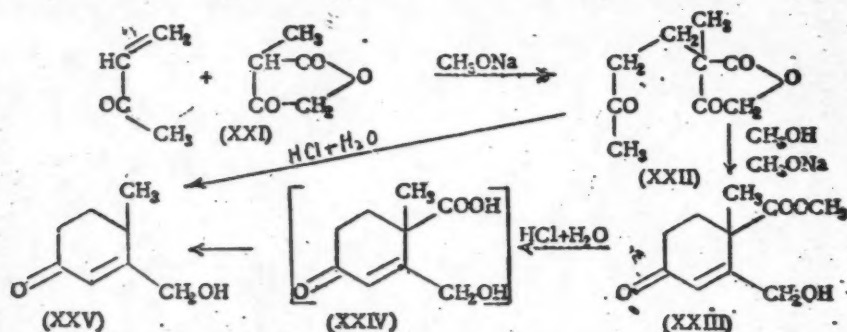
The diketolactone (XXII) undergoes cyclization under the influence of sodium methoxide in methanol, with simultaneous opening of the lactone ring, giving the ketohydroxy-ester (XXIII). The keto-alcohol (XXV) is also formed, as a result of a process of consecutive hydrolysis and decarboxylation of the ester (XXIII). As was expected, the compounds (XXII) and (XXIII) readily afford the keto-alcohol (XXV) when boiled with hydrochloric acid.

The starting substances for the above-described reactions were prepared as follows: methyldihydroresorcinol

(IV) was obtained in two ways: 1) from acrylic ester through glutaric acid and methyl hexan-3-one-6-carboxylate (XXVII), and 2) by methylation of dihydroresorcinol (XXVIII):

(XXVIII)   (IV)   (XXVII)

The former method has already been described [5, 6], but we have introduced a number of improvements. The latter method has not been described previously, except for a short note by Robinson [7], which appeared while we were preparing the present paper for publication. 5-Carbomethoxypent-1-en-3-one (XIV) was synthesized from the methiodide (XXX), obtained from 5-piperidinopentan-3-one-1-carboxylic acid (XXIX) [8]:

$$HCl \cdot C_5H_{10}NCH_2CH_2COCH_2CH_2COOH \xrightarrow{CH_3OH}{HCl} C_5H_{10}NCH_2CH_2COCH_2CH_2COOCH_3$$

(XXIX)

$$\downarrow CH_3I$$

$$CH_2 = CHCOCH_2CH_2COOCH_3 \longleftarrow CH_3I \cdot C_5H_{10}NCH_2CH_2COCH_2CH_2COOCH_3$$

(XIV)   (XXX)

We originally intended to prepare the vinyl ketone (XXXI) from pentan-4-one-1-carboxylic acid (XXXII); the Mannich reaction took place with participation of the methylene group, giving the isomeric vinyl ketone (XXXIII):

$$(C_2H_5)NH \cdot HCl + CH_2O + CH_3COCH_2CH_2CH_2COOH \longrightarrow CH_3CO-C-CH_2CH_2COOCH_3$$

(XXXII) $$\underset{CH_2}{\overset{\|}{}}$$ (XXXIII)

$$CH_2=CHCOCH_2CH_2CH_2COOCH_3 \quad (XXXI)$$

EXPERIMENTAL

But-en-3-one (III), b.p. 79-80°, n_D^{20} 1.4460, was prepared by hydration of vinylacetylene [9].

5-Piperidinopentan-3-one-1-carboxylic acid (XXIX), m.p. 145-146°, was prepared by the reaction of levulinic acid with piperidine hydrochloride and paraldehyde [8].

Dihydroresorcinol (XXVIII), m.p. 104-105°, was prepared by hydrogenation of resorcinol [10].

Tetrinic acid (XXI), m.p. 189-190°, was synthesized from 4-bromobutan-3-one-2-carboxylic ester [11].

Hexan-5-one-2-carboxylic acid (X), b.p. 123-126°/3 mm (semicarbazone, m.p. 140-141°) was obtained by hydrolysis of the condensation product of acetoacetic and methacrylic esters [2].

5-Carbomethoxypent-3-one (XIV).

Ten g of 5-piperidinopentan-3-one-1-carboxylic acid hydrochloride (XXIX) is dissolved in 40 ml of methanol, and the solution is saturated with dry hydrogen chloride. Volatile products are removed by vacuum distillation, and the residue is treated with 20 g of saturated aqueous potassium carbonate. The oil is extracted with ether, the extract is dried with magnesium sulfate, and the solvent is distilled off. Methyl iodide (15 g) is added to the residue, and the methiodide so obtained is distilled in vacuum, when it decomposes with formation of 5-carbomethoxypent-1-en-3-one (XIV), b.p. 99-100°/15 mm, n_D^{20} 1.4491; yield 3.2 g.

Found %: C 58.82; 58.62; H 7.30; 7.02. $C_7H_{10}O_3$. Calculated %: C 59.1; H 7.0.

Condensation of acetoacetic ester with methyl acrylate.

A solution of 24 g of methyl acrylate in 36 g of acetoacetic ester is added with stirring during 5 min. to a solution of sodioacetoacetic ester, prepared from 0.5 g of sodium and 36 g of acetoacetic ester. The temperature of the mixture rises after 1-2 min., and continues to do so for 2 hours, after which it is heated on a water bath at 70-80° for

90 min., when 30 ml of 1:1 hydrochloric acid is added. The oily layer which separates is dried with magnesium sulfate, and distilled; yield 46 g of 5-carbomethoxy-3-carboethoxypentan-2-one, b.p. 142-144°/10 mm [12].

Pentan-4-one-1-carboxylic acid (XXXII).

A mixture of 46 g of 5-carbomethoxy-3-carboethoxypentan-2-one and 200 ml of 1:1 hydrochloric acid is boiled under reflux for 5 hours, the hydrochloric acid layer is separated, and the residue is distilled in vacuum, giving 20 g of pentan-4-one-1-carboxylic acid (XXXII), b.p. 142-144°/10 mm [13].

Methyl 3-methylenopentan-4-one-1-carboxylate (XXXIII).

A mixture of 10 g of pentan-4-one-1-carboxylic acid, 8.5 g of diethylamine hydrochloride, and 2.5 g of paraformaldehyde was heated for 40 min. at 110-115° at 10 mm pressure, after which it is dissolved in 50 ml of dry methanol, and the solution is saturated with hydrogen chloride. The solvent is then distilled off, and the residue is treated with 10 ml of saturated aqueous potassium carbonate. The oil separating is dissolved in ether, the solution is dried with magnesium sulfate, the solvent is distilled off, and the residue is vacuum distilled, giving 4.5 g of methyl 3-methylenopentan-4-one-1-carboxylate (XXXIII), b.p. 77-81°/3 mm., n_D^{20} 1.4510.

Found %: C 61.31; 61.54; H 7.77; 7.98. $C_9H_{12}O_3$. Calculated %: C 61.54; H 7.69.

Oxidation of methyl 3-methylenopentan-4-one-1-carboxylate (XXXIII).

Two g of methyl 3-methylenopentan-4-one-1-carboxylate is heated to 90° with 20 ml of 20% nitric acid, when the solution begins to boil, with evolution of oxides of nitrogen. It is kept at the boil for 2 hours, and then evaporated to dryness in vacuum. The crystalline residue is succinic acid (0.7 g), m.p. 182-183° after recrystallization from benzene.

Preparation of propane-1,1,3-tricarboxylic ester (XXVI).

A solution of 120 g of methyl acrylate in 120 g of malonic ester is added drop by drop, during 90 min., with constant stirring, to a solution of sodiomalonic ester, prepared from 0.5 g of sodium and 240 g of malonic ester; the reaction flask is cooled, so as to maintain the temperature of the reaction mixture at 38-40°. The system is allowed to stand for 12 hours, and the product is washed with 100 ml of 1:10 hydrochloric acid, dried with magnesium sulfate, and distilled in vacuum, giving 266 g of propane-1,1,3-tricarboxylic ester (XXVI), b.p. 145-148°/14 mm [14]; 180 g of unreacted malonic ester is recovered.

Preparation of glutaric acid.

A mixture of 250 g of propane-1,1,3-tricarboxylic ester and 1.5 liters of 1:1 hydrochloric acid is boiled under reflux for 6 hours, the hydrochloric acid is distilled off in vacuum, and the residue is fractionally distilled, giving 110 g of glutaric acid, b.p. 165-170°/4 mm, m.p. 95-96° [12].

Preparation of glutaric anhydride.

A mixture of 110 g of glutaric acid and 250 ml of acetic anhydride is boiled under reflux for 2 hours, acetic anhydride and acetic acid are distilled off under reduced pressure, and 250 ml of fresh acetic anhydride is added to the residue, which is boiled for a further 2 hours under reflux. Excess of acetic anhydride and acetic acid are distilled off in vacuum, and the residue is fractionally distilled, giving 80 g of glutaric anhydride, b.p. 148-150°/12 mm, m.p. 56-57° [5].

Monomethyl glutarate.

A mixture of 80 g of glutaric anhydride and 45 g of anhydrous methanol is boiled under reflux for 1 hour, excess of methanol is distilled off, and the residue is vacuum distilled, giving 62 g of monomethyl glutartate, b.p. 140-142°/10 mm [5].

Chloride of 3-carbomethoxybutyric acid.

A mixture of 62 g of monomethyl glutarate and 150 g of thionyl chloride is heated on the water bath at 50-60° until evolution of hydrogen chloride ceases (2 hr.), when excess of thionyl chloride is distilled off, and the residue is distilled in vacuum, giving 60 g of 3-carbomethoxybutyryl chloride, b.p. 92-93°/9 mm [5].

Methyl hexan-3-one-6-carboxylate (XXVII).

22 g of finely powdered cadmium chloride is added during 8 minutes, with constant stirring, and cooling in

313

ice, to a Grignard reagent prepared from 5 g of magnesium, 30 g of ethyl bromide, and 80 ml of absolute ether. Stirring is continued at room temperature for 1 hour, after which 40 ml of ether are distilled off, and 80 ml of dry benzene is added to the residue. A solution of 24 g of 3-carbomethoxybutyryl chloride in 20 ml of dry benzene is added to the suspension so obtained, during 20 min., and with energetic stirring, after which it is heated on a boiling water bath for 1 hour with stirring. 30 g of ice and 50 ml of 10% hydrochloric acid are then added, the ether-benzene layer is separated, and the aqueous layer is extracted with benzene. The combined extracts are dried with magnesium sulfate, the solvents are distilled off, and the residue is fractionally distilled in vacuum, giving 19 g of methyl hexan-3-one-6-carboxylate (XXVII), b.p. 97-98°/10 mm, n_D^{20} 1.4303 [5].

Preparation of 2-methyldihydroresorcinol (IV).

a) 2.4 g of methyl hexan-3-one-6-carboxylate (XXVII) is added during 2 min. with constant stirring to a suspension of sodium methoxide, prepared from 0.7 g of sodium and 0.9 g of absolute methanol in 30 ml of absolute ether. The precipitate formed is collected after 2 hours, washed with ether, treated with 10 ml of 1:1 hydrochloric acid, and washed with water. Recrystallization from methanol gives 1.7 g of 2-methyldihydroresorcinol (IV), m.p. 208-209° [5].

b) 11.2 g of dihydroresorcinol, followed by 16 g of methyl iodide, are added to a solution of sodium methoxide, prepared from 2.3 g of sodium and 35 ml of anhydrous methanol, and the mixture is boiled on the water bath for 1 hour, after which methanol is distilled off in vacuum, and 10 ml of water is added to the residue. The crystalline precipitate formed is collected, washed with water, and recrystallized from methanol, giving 5 g of 2-methyldihydroresorcinol, m.p. 209-210°, not depressing the m.p. of the above product.

c) 2 g of dihydroresorcinol, followed by 3 g of methyl iodide, are added to a solution of 1 g of potassium hydroxide in 7 ml of anhydrous methanol, and the mixture is boiled for 40 min., after which the operations described in (b) above are performed, giving 0.4 g of 2-methyldihydroresorcinol, m.p. 209-210°, not depressing the m.p. of a known sample.

Condensation of 2-methyldihydroresorcinol (IV) with but-1-en-3-one (III).

A solution of sodium methoxide, prepared from 0.1 g of sodium and 30 ml of absolute methanol, is heated on a water bath with 3 g of 2-methyldihydroresorcinol until the latter is all dissolved, when 2 g of but-1-en-3-one is rapidly added, and heating is continued at 55-60° for 4 hours, after which the solution is made neutral by addition of concentrated hydrochloric acid, cooling with ice. The solvent is distilled off, and the residue is treated with 3 ml of water; unreacted 2-methyldihydroresorcinol (0.2 g) is filtered off, and 3 ml of saturated aqueous sodium carbonate are added to the filtrate. The oily product is extracted with ether, and the ethereal solution is dried with magnesium sulfate. The ether is then distilled off, and the residue is vacuum distilled, giving 2 g of the triketone (V), b.p. 118-125°/0.1 mm., n_D^{20} 1.4910.

Found %: C 66.92; 67.04; H 8.30; 8.51; $C_{11}H_{16}O_3$. Calculated %: C 67.31; H 8.17.

The alkaline solution remaining after ether extraction is made acid to Congo red with concentrated hydrochloric acid, the oil separating is extracted with ether, the extract is dried with magnesium sulfate, and the ether is distilled off; the crystalline residue is recrystallized from ether, giving 0.05 g of keto-acid (VIII), m.p. 48-49°.

Found %: C 67.06; 67.05; H 8.57; 8.32. $C_{11}H_{16}O_3$. Calculated %: C 67.31; H 8.17.

Equivalent found by titration 194. $C_{11}H_{16}O_3$. Calculated equivalent 196.

The substance gives no coloration with $FeCl_3$. Its semicarbazone melts at 205-208°, with decomposition.

Found %: N 17.24; 16.97. $C_{12}H_{19}O_3N_3$. Calculated %: N 16.7.

Ozonation of the keto-acid (VIII).

Oxygen containing 6% of ozone is passed for 4 hours into a solution of 2 g of the unsaturated keto-acid (VIII) in 20 ml of dry chloroform, and 20 ml of 5% perhydrol is then added, after which the mixture is boiled with vigorous stirring for 12 hours. The chloroform and water are then distilled off in vacuum, leaving a crystalline residue, from which 0.7 g of succinic acid, m.p. 182-183° (recrystallized from benzene), and 0.2 g of hexan-2-one-5-carboxylic acid semicarbazone, m.p. 140-141° (from methanol), not depressing the m.p. of known specimens of the compounds, are obtained.

Attempts at cyclization of the triketone (V).

Experiment 1. 1 g of triketone (V) was dissolved in 2 ml of concentrated sulfuric acid, cooling with ice. After standing for 2 hour at room temperature the solution was poured on ice, and the resulting solution was extracted with benzene. The benzene extract was dried with magnesium sulfate, the solvent was distilled off, and the residue was recrystallized from ether, giving the unsaturated keto-acid (VIII), m.p. 48-49°.

Experiment 2. A mixture of 2 g of triketone (V) and 1 g of oxalic acid was heated at 110-115° for 1 hour, under reflux, the product was treated with 2 g of saturated sodium carbonate solution, and extracted with benzene. The benzene was distilled off, leaving 0.2 g of a thick oil, from which a semicarbazone, m.p. 238-241°, was obtained, not depressing the m.p. of a specimen of the semicarbazone of octalin (VI). The alkaline solution remaining after benzene extraction was made acid to Congo red with concentrated hydrochloric acid, and extracted with benzene. The solvent was distilled off, leaving a crystalline residue, recrystallization of which from ether gave 1 g of the unsaturated keto-acid (VIII), m.p. 48-49°.

Experiment 3. A solution of 0.2 g of sodium hydroxide in 5 ml of water was added to 1 g of triketone (V) dissolved in 5 ml of methanol, the mixture was allowed to stand for 1 hour at room temperature, and then made acid to Congo red with concentrated hydrochloric acid, and extracted with benzene. The solvent was distilled off from the extract, and the residue was recrystallized from ether, giving 0.5 g of unsaturated keto-acid (VIII), m.p. 48-49°.

Experiment 4. 2 g of triketone (V) was added to a solution of sodium methoxide prepared from 0.1 g of sodium and 8 ml of methanol, the solution was made neutral with concentrated hydrochloric acid after 24 hour at room temperature, 0.5 g of sodium carbonate was added, and the solution was extracted with benzene. The solvent was distilled off, and the residue was fractionally distilled, giving 1 g of product of b.p. 132-138°/2 mm, n_D^{29} 1.5070, from which 0.3 g of a semicarbazone, m.p. 239-242°, was obtained, not depressing the m.p. of a specimen of semicarbazone of octalin (VI).

Experiment 5. A mixture a 2 g of triketone (V) with 5 ml of absolute methanol and 2 drops of piperidine was left for 2 days at room temperature, the volatile substances were distilled off, and the residue was distilled in vacuum, giving 1.2 g of a substance of b.p. 132-137°/2 mm, n_D^{29} 1.5505, from which 0.2 g of a semicarbazone of m.p. 240-242° was obtained, not depressing the m.p. of the semicarbazone of octalin (VI).

Experiment 6. A mixture of 2 g of triketone (V) with 0.4 g of anhydrous oxalic acid was heated for 15 min. at 130-140°/15 mm., the cooled product was treated with 3 ml of saturated sodium carbonate solution, and extracted with benzene. The solvent is distilled off, and the residue is distilled in vacuum; the fraction boiling at 122-126°/2 mm., n_D^{29} 1.5235, partially crystallizes, and recrystallization from light petroleum affords 0.2 g of 1,6-diketo-9-methyl-Δ^5-octalin (VI), m.p. 47-48°, the bis-semicarbazone of which melts at 244-245°, with decomposition [3].

The alkaline solution remaining after extraction of neutral products was made acid to Congo red with concentrated hydrochloric acid, and was extracted with benzene. The benzene solution was dried with magnesium sulfate, and the solvent was distilled off, leaving a crystalline residue from which 0.2 g of unsaturated keto-acid (VIII), m.p. 48-49° (from ether), was obtained.

Experiment 7. 3.7 g of triketone (V) was heated at 100° for 5 min. with 3 g of phosphorus pentoxide, and the cooled product was treated with excess of concentrated aqueous sodium carbonate, the oil forming was extracted with benzene, the benzene solution was dried with sodium sulfate, and the benzene was distilled off in vacuum, leaving 2.3 g of chromanone (XII), b.p. 121-124°/2 mm., n_D^{29} 1.5338.

Found %: C 74.06; 74.05; H 8.19; 8.05. $C_{11}H_{14}O_2$. Calculated %: C 74.2; H 7.95.

The product did not undergo hydrogenation in methanol solution with palladium on charcoal as catalyst. It instantly decolorizes permanganate.

Experiment 8. A solution of 2.9 g of triketone (V) with 3 drops of piperidine in 20 ml of dry benzene was boiled for 7 hours, the solvent and the water formed were distilled off in vacuum, and the residue was fractionated, giving 1.3 g of oil of b.p. 130-135°/3 mm., n_D^{29} 1.5370, from which was obtained 0.3 g of 1,6-diketo-9-methyl-Δ^5-octalin (VI), m.p. 47-48°.

Experiment 9. A mixture of 2.9 g of triketone (V) and 0.5 g of piperidine butyrate was heated on a water bath at 90-95°/15-20 mm., for 4 hours, the product was made acid to Congo red with 1:1 hydrochloric acid, and the solution was extracted with benzene, the benzene extract was dried with magnesium sulfate, the solvent was

distilled off, and the residue was distilled in vacuum, giving 2.1 g of oil of b.p. 128-131°/3 mm., n_D^{20} 1.5320, from which 1.5 g of 1,6-diketo-9-methyl-Δ^5-octalin (VI), m.p. 47-48°, was obtained.

Hydrogenation of 1,6-diketo-9-methyl-Δ^5-octalin (VI).

0.1 g of 1,6-diketo-9-methyl-Δ^5-octalin (VI) was hydrogenated in methanol solution, with palladized charcoal (5% Pd) as catalyst. The reaction was completed in 17 min., giving 0.06 g of cis-1,6-diketo-9-methyldecalin (II), m.p. 66-67°, not depressing the m.p. of a known specimen obtained by hydrolysis of 1-keto-6-methoxy-9-methyl-Δ^5-octalin (I) [1].

Hydrolytic decomposition of 1,6-diketo-9-methyl-Δ^5-octalin (VI).

0.4 g of 1,6-diketo-9-methyl-Δ^5-octalin (VI) and 0.3 g of sodium hydroxide in 5 ml of water was boiled under reflux for 1 min., and the cooled solution was extracted with benzene. The aqueous layer was then made acid to Congo red with concentrated hydrochloric acid, and was again extracted with benzene, this extract being dried with sodium sulfate, and the solvent was distilled off. The residual oil was a mixture of carboxylic acids, from which a semicarbazone, m.p. 198-199° (from methanol) was obtained.

Found %: N 16.64; 17.02. $C_{12}H_{19}O_3N_3$. Calculated %: N 16.7.

This semicarbazone slightly depressed the m.p. of the semicarbazone of the unsaturated keto-acid (VIII).

1,6-Diketo-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI).

2.5 g of 2-methyldihydroresorcinol (IV) is dissolved in a solution of 0.1 g of sodium in 8 ml of anhydrous methanol, followed by 2 g of 5-carbomethoxypent-1-en-3-one (XIV), and the mixture is boiled under reflux for 3 hours, the solvent is distilled off, the residue is made neutral with 1:1 hydrochloric acid, and 2 g of saturated aqueous sodium carbonate is added. The oil separating is extracted with benzene, and the extract is dried with magnesium sulfate. The solvent is distilled off, leaving 3.6 g of a viscous oil (n_D^{20} 1.4850), distilling over at 195-202°/0.05 mm., with considerable decomposition. A mixture of 3.6 g of undistilled condensation product (XV) with 0.4 g of anhydrous oxalic acid is heated at 140-150°/15 mm for 30 min., and 10 ml of water are added to the cooled product, giving a crystalline precipitate, recrystallization of which from methanol affords 2.4 g of 1,6-diketo-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI), m.p. 172-173°.

Found %: C 66.29; 66.00; H 7.02; 7.15. $C_{13}H_{15}O_4$. Calculated %: C 66.11; H 6.8.

The product does not give any coloration with $FeCl_3$. It neutralizes 2 molecules of alkali when titrated hot.

Equivalent found by titration 115. $C_{13}H_{15}O_4$. Calculated equivalent 118.

Hydrolytic decomposition of the product of condensation of 2-methyl-dihydroresorcinol (IV) with 5-carbomethoxypent-1-en-3-one (XIV).

0.5 g of the above-described crude condensation product (XV) is boiled for 3 hours under reflux with 10 ml of concentrated hydrochloric acid, which is then removed in vacuum, leaving 0.25 g of the ketodicarboxylic acid (XVIII), m.p. 150-152° (recrystallized from water).

Found %: C 61.30; 61.40; H 7.32; 7.33. $C_{13}H_{18}O_5$. Calculated %: C 61.4; H 7.1

Equivalent found by titration 126. $C_{13}H_{18}O_5$. Calculated equivalent 127.

Hydrolytic decomposition of 1,6-dikto-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI).

0.4 g of 1,6-diketo-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI) is boiled with 15 ml of 1:1 hydrochloric acid under reflux for 2 hours, the hydrochloric acid is removed in vacuum, and the residue is recrystallized from water, giving 0.3 g of the ketodicarboxylic acid (XVIII), m.p. 150-152°, not depressing the m.p. of the sample obtained in the preceding experiment.

Esterification of 1,6-diketo-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI).

A solution of 3.4 g of 1,6-diketo-9-methyl-5-carboxymethyl-Δ^5-octalin (XVI) in 40 ml of absolute methanol is saturated with dry hydrogen chloride, and left for several days at room temperature. The methanol and hydrogen chloride are then distilled off in vacuum, and the residue is treated with 5 g of saturated aqueous sodium carbonate. The oil is extracted with benzene, the benzene solution is dried with magnesium sulfate, and the solvent is distilled off. The residue gives 3.2 g of diester (XIX), b.p. 172-173°/3 mm., n_D^{20} 1.4905.

Found %: C 63.40; 63.44; H 7.94; 7.97. $C_{15}H_{22}O_5$. Calculated %: C 63.8; H 7.9.

Hydrolysis of the dimethyl ester (XIX).

0.3 g of dimethyl ester (XIX) is boiled for 3 hours under reflux with 10 ml of 1:1 hydrochloric acid, which is then distilled off in vacuum, leaving 0.2 g of acid (XVIII), m.p. after recrystallization from water 150-152°, not depressing the m.p. of a known specimen of the unsaturated ketodicarboxylic acid (XVIII).

Ozonation of the dimethyl ester (XIX).

Oxygen containing 6% of ozone is passed for 4 hours through a solution of 1.5 g of dimethyl ester (XIX) in 25 ml of dry chloroform, 20 ml of 5% perhydrol is added, and the mixture is boiled, with vigorous stirring, for 12 hours, after which the chloroform and water are boiled off in vacuum. The residue is boiled for 2 hours with 20 ml of 1:1 hydrochloric acid, which is then distilled off in vacuum, and the residue is fractionated by recrystallization from water and benzene, giving 0.4 g of succinic acid, m.p. 182-183°, not depressing the m.p. of a known sample of succinic acid, and 0.5 g of heptan-3-one-1,6-dicarboxylic acid (XX), m.p. 107-109°.

Found %: C 53.47; 53.42; H 7.34; 7.22. $C_9H_{14}O_5$. Calculated %: C 53.5; H 7.3.

Equivalent found by titration 101.1. $C_9H_{14}O_5$. Calculated equivalent 100.

The semicarbazone melts at 171-172° (recrystallized from methanol). .

Found %: N 16.60; 16.43. $C_{12}H_{17}O_5N_3$. Calculated %: N 16.2.

Condensation of tetrinic acid (XXI) with but-1-en-3-one (III)

2.4 g of tetrinic acid [1,3-lactone of butan-2-on-1-ol-3-carboxylic acid] (XXI), followed by 2.5 g of but-1-en-3-one (III) are added to a solution obtained from 0.05 g of sodium and 10 ml of absolute methanol, and the mixture is boiled for 3.5 hours under reflux. The methanol is then distilled off in vacuum, the residue is made neutral (to Congo red) with 1:1 hydrochloric acid, 2 g of sodium carbonate is added, the oil is extracted with benzene, the solution is dried with sodium sulfate, and the solvent is distilled off, leaving 2.2 g of the diketone (XXII), b.p. 130-131°/3 mm., n_D^{20} 1.4710.

Found %: C 58.58; 58.80; H 6.42; 6.65. $C_9O_4H_{12}$. Calculated %: C 58.69; H 6.52.

The substance did not give Tserevitinov's reaction for active hydrogen. It gave a bis-semicarbazone, m.p. 205-206°, with decomposition.

Found %: N 28.20; 28.08. $C_{11}H_{18}O_4N_6$. Calculated %: N 28.2.

Preparation of the unsaturated ketones (XXIII) and (XXV).

The reaction of condensation of tetrinic acid with but-1-en-3-one was conducted as before, except that the amount of sodium was increased to 0.1 g. In this way, 2.4 g of tetrinic acid gave 2.6 g of crude product, from which two fractions were obtained:

Fraction I, 0.2 g, b.p. 80-85°/3 mm
Fraction II, 1.6 g, b.p. 100-115°/3 mm

Recrystallization of Fraction I from methanol gave 0.1 g of crystalline alcohol (XXV), m.p. 65-66°, which instantly decolorized aqueous permanganate.

Found %: C 68.11; 67.94; H 8.74; 8.74. $C_8H_{12}O_2$. Calculated %: C 68.4; H 8.8.

Found %: OH 11.76. $C_8H_{11}O(OH)$. Calculated %: OH 12.15.

Fraction II gave 0.6 g of keto-ester (XXIII), m.p. 90-91° (from methanol). The substance did not neutralize alkalis, and instantly decolorized permanganate solution.

Found %: C 60.30; 60.35; H 7.05; 6.96. $C_{10}H_{14}O_4$. Calculated %: C 60.6; H 7.1.

Found %: OH 8.3; $C_{10}H_{13}O_3(OH)$. Calculated %: OH 8.7.

Hydrolytic decomposition of the lactone (XXII).

A mixture of 1 g of lactone (XXII) and 15 ml of concentrated hydrochloric acid was distilled, under atmospheric

pressure; evolution of carbon dioxide was observed, and the distillate crystallized, giving 0.3 g of keto-alcohol, m.p. 65-66° (from aqueous methanol), not depressing the m.p. of a specimen of the above-described keto-alcohol (XXV).

Hydrolytic decomposition of the keto-ester (XXIII).

Under similar conditions to those of the preceding experiment the keto-ester (XXIII) gave 0.3 g of a substance of m.p. 65-66° (from aqueous methanol), not giving any depression with the above keto-alcohol (XXV).

Attempted cyclization of the lactone (XXII).

4 g of lactone (XXII) is heated for 20 minutes with 2 g of oxalic acid at 140-150°, and the product was neutralized with saturated sodium carbonate solution. The oil was extracted with benzene, the extract was dried with magnesium sulfate, and fractionally distilled.

Fraction I, 0.4 g, b.p. 80-90°/3 mm.
Fraction II, 0.5 g, b.p. 100-130°/3 mm, n_D^{20} 1.4910.
Fraction III, 1.7 g, b.p. 130-135°/3 mm, n_D^{20} 1.4928.

Fraction I gave 0.2 g of the keto-alcohol (XXV), m.p. 65-66°, not depressing the m.p. of the previously obtained specimens. Fraction III appeared to be the impure cyclization product.

Found %: C 61.27; 60.98; H 6.69; 6.76. Calculated for lactone (XXII)%: C 58.7; H 6.52.
Calculated for the product of cyclo-dehydration of lactone (XXII)%: C 65.1; H 6.03.

This substance is readily converted by boiling with hydrochloric acid into the above-described keto-alcohol (XXV).

SUMMARY

1. A study has been made of the condensation of the vinyl ketones (III) and (XIV) with methyldihydroresorcinol, and of the cyclization of the resulting dihydroresorcinol derivatives (V) and (XV) into the diketo-octalin derivatives (VI) and (XVI):

R = H or CH₂COOH₃
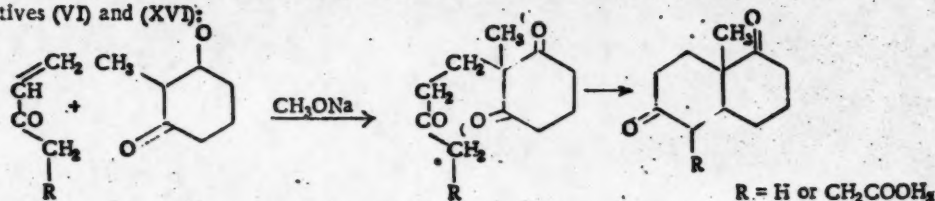
2. The triketones (V) and (XV), similarly to the octalins (VI) and (XVI), readily undergo hydrolytic decomposition, with ring opening and formation of the intermediate keto-acids (VII) and (XVII), which then undergo ring closure, giving the cyclohexenone carboxylic acids (VIII) and (XVIII). Condensation of but-1-en-3-one with tetrinic acid (XXI) affords the lactone (XXII), cyclization of which gives the ester (XXIII) and the alcohol (XXV). The lactone (XXII) and the ester (XXIII) are readily converted into the alcohol (XXV) by boiling with hydrochloric acid, by decarboxylation of the hydroxyketo-acid (XXIV).

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*See Consultants Bureau translation, p. 685.

SYNTHESIS OF HYDROCARBONS OF THE CYCLOBUTANE SERIES

PART 2. 1-METHYL-3-ETHYLCYCLOBUTANE AND DI-(3-METHYLCYCLOBUTYL) METHANE.

B. A. Kazansky and M. Yu. Lukina

The synthesis of 1-methyl-3-ethylcyclobutane was effected analogously to that of 1,3-dimethylcyclobutane [1]. The starting substance was also 1-methylcyclobutane-3-carboxylic acid, prepared from sodiomalonic ester and 1-chloro-3-bromo-2-methylpropane, through 4-chloro-3-methyl-butane-1,1-dicarboxylic ester and 1-methylcyclobutane-3,3-dicarboxylic acid.

1-Methylcyclobutane-3-carboxylic acid, however, does not give the aldehyde, but affords the ketone 3-acetyl-1-methylcyclobutane, which was reduced by Kizhner's method to the hydrocarbon 1-methyl-3-ethylcyclobutane:
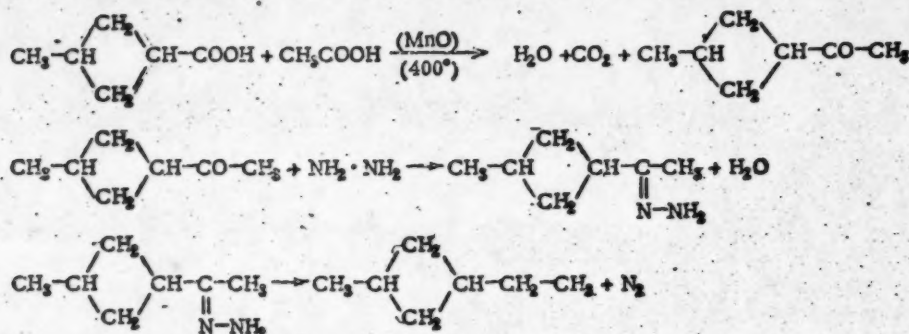
The preparation of 3-acetyl-1-methylcyclobutane, and its conversion into the hydrocarbon, proceeded more smoothly, and with higher yields, than in the case of 1-formyl-3-methylcyclobutane and its conversion into 1,3-dimethylcyclobutane.

A certain amount of a substance of higher boiling point was obtained in the synthesis of both 3-acetyl- and 3-formyl- 1-methylcyclobutane; this product could have been di-(3-methylcyclobutyl) ketone, which could readily be formed by the reactions:
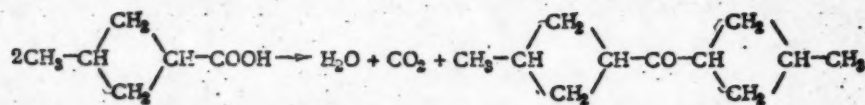
This supposition was checked by converting pure 1-methylcyclobutane-3-carboxylic acid into the ketone, at 420° in the presence of manganous oxide. The ketone so obtained had the same b.p. of 215-220°, identical with that of the ketone obtained as a by-product of the above syntheses, which could, obviously, be a mixture of the three isomers:

(I) cis-cis-isomer   (II) cis-trans-isomer

(III) trans-trans-isomer
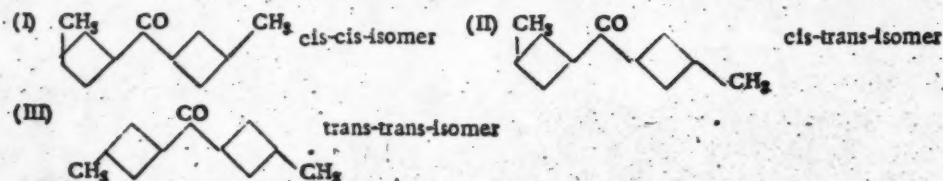
The separation of the stereoisomers was not attempted, the mixture being converted by Kizhner's method into a mixture of hydrocarbons. The stereoisomeric hydrocarbons were also not separated, in view of their small amount, and of the complexity of the separation process.

The stereoisomeric 1-methyl-3-ethylcyclobutanes obtained by Kizhner's method from 3-acetyl-1-methylcyclobutane were separated by fractional distillation, using an efficient column, into cis- and trans-isomers, obtained, similarly to the 1,3-dimethylcyclobutanes, in a fairly pure state. The determination of their space configuration was performed in accordance with the principles advanced in the preceding paper [1].

EXPERIMENTAL

1. 3-Acetyl-1-methylcyclobutane $CH_3-CH\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}CH-COCH_3$
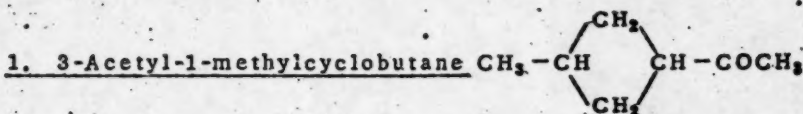
A mixture of 23 g (0.2 mol.) of 1-methylcyclobutane-3-carboxylic acid and 51.5 g (0.86 mol.) of glacial acetic acid was passed at the rate of 16 ml per hour through a tube containing 50 g of freshly reduced manganous oxide at 420°, prepared as described in the previous paper [1]. Unreacted acid was separated from the reaction products by shaking with aqueous sodium carbonate. The alkaline solution was extracted with ether, which was added to the ketone layer previously separated, the mixture was dried with magnesium sulfate, and the ether and a small amount of acetone were distilled off. The residue was fractionated in a Favorsky flask:

Fraction I, wt. 14.4 g, b.p. 146-156°.
Fraction II, wt. 1.4 g, b.p. 156-220°.

The alkaline solution was made acid with mineral acid, and the acidic products liberated were extracted with ether. The extract was dried, the ether was distilled off, and the residue was fractionally distilled, giving 4.2 g of methylcyclobutanecarboxylic acid, b.p. 198-203°. Thus the yield of 3-acetyl-1-methylcyclobutane was 63.7%, on the basis of acid taken, and 78% on the basis of acid actually used.

The yields obtained under identical conditions, but at a temperature of 412°, were lower, viz., 69.8, 71, and 70.4% of theoretical on acid actually used in the reaction, or 55-56% on acid taken in the mixture.

Altogether, 98.4 g of 3-acetyl-1-methylcyclobutane was obtained.

The ketone reacted less readily than did the aldehyde with sodium bisulfite, but it gave a voluminous precipitate of bisulfite compound after standing for several hours. The compound, which crystallizes in fine needles, was collected and washed with pentane, and the ketone regenerated from it was distilled from a Favorsky flask; it consisted evidently of a mixture of cis- and trans-isomers, which could not be separated. The redistilled ketone had the following properties: b.p. 144-149°/758 mm., n_D^{20} 1.4281, d_4^{20} 0.8755, MR_D found 32.95, calculated for $C_7H_{12}O$ 32.34 (increment of MR_D 0.61).

Found %: C 74.72; 74.72; H 10.97; 11.05. $C_7H_{12}O$. Calculated %: C 74.94; H 10.79.

Semicarbazone of 3-acetyl-1-methylcyclobutane
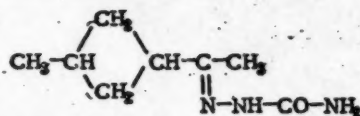
This was prepared in exactly the same way as the semicarbazone of 3-formyl-1-methylcyclobutane [1]. It melted at 125° after 5 recrystallizations from aqueous methanol, and it probably corresponds to that of the stereo-isomers of the ketone which predominates in the reaction product.

Found %: N 24.46. $C_8H_{15}ON_3$. Calculated %: N 24.94.

2,4-Dinitrophenylhydrazone of 3-acetyl-1-methylcyclobutane
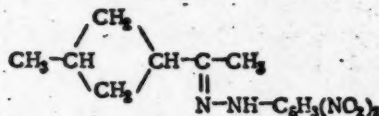
This was prepared in the same way as the corresponding derivative of 3-formyl-1-methylcyclobutane [1]. It melted at 140° after 4 recrystallizations from ethanol.

Found %: N 18.97; 18.82. $C_{12}H_{16}N_4O_4$. Calculated %: N 19.25.

2. 1-Methyl-3-ethylcyclobutane $CH_3 - CH \overset{\displaystyle CH_2}{\underset{\displaystyle CH_2}{\big<}} CH - C_2H_5$

A solution of 74 g (1.47 mol.) of hydrazine hydrate in 70 ml of ethanol was added to 81.8 g (0.73 mol) of 3-acetyl-1-methylcyclobutane dissolved in 80 ml of ethanol, and the mixture was boiled for 4 hours under reflux. The aqueous layer formed was removed, and the hydrazone was dried with anhydrous potassium hydroxide, at room temperature initially, and later on a boiling water bath. The hydrazone was separated from the potassium hydroxide solution, and was decomposed, without any preliminary distillation, in exactly the same way as the hydrazone of 3-formyl-1-methylcyclobutane [1], giving 53.8 g of 1-methyl-3-ethylcyclobutane, a yield of 75.4% calculated on the amount of 3-acetyl-1-methylcyclobutane taken. The product was dried over fused calcium chloride, and was distilled from metallic sodium, giving a product of the following properties: b.p. 87.9-91.6°/755 mm., n_D^{20} 1.4019, d_4^{20} 0.7262, MR_D found 32.88, calculated for C_7H_{14} 32.32 (increment of MR_D 0.56).

The hydrocarbon so obtained was a mixture of the trans- and the cis-isomer, and, as in the case of 1,3-dimethyl-cyclobutane, separation into the individual stereoisomers was effected by fractional distillation of 50.25 g (70.4 ml) of the hydrocarbon, using a column of 50 theoretical plates, with an output of 1 ml per hour, adding 15 ml of octane (n_D^{20} 1.3970) to the distilling flask after 60 ml of distillate had been received.

Two fractions, boiling at about 88° and 91° at 760 mm, were obtained, as well as an intermediate fraction, which was returned for further fractionation. The fractions shown in Table 1 were finally collected.

TABLE 1

No. of fraction	B.p., °C	Pressure, mm	Amount g	Amount ml
1	76.3 - 87.5	760	2.2	3.2
2	87.5 - 87.9	760	4.25	6.3
3	87.9 - 88.1	760	17.4	24.3
4	88.1 - 91.0	760	13.5	18.5
5	91.0 - 91.1	760	7.8	10.8
6	91.1 - 92.0	760	2.0	3.0

It may be concluded from the results shown in Table 1 that we had separated two individual hydrocarbons, boiling at 87.9-88.1° and at 91.0-91.1°/760 mm, and an intermediate fraction, being a mixture of these fractions, distilling over at 88.1-91.0°. The fraction of b.p. 87.9-88.1° may be assumed, on the grounds given in our previous paper [1], to be the trans-isomer, and the fraction of b.p. 91.0-91.1° would be the cis-isomer of 1-methyl-3-ethylcyclobutane.

Trans-1-Methyl-3-ethylcyclobutane: b.p. 87.9-88.1°/760 mm, n_D^{20} 1.4005, d_4^{20} 0.7224, MR_D found 32.96, calculated for C_7H_{14} 32.32 (MR_D increment 0.64).

Found %: C 85.61; 85.64; H 14.39; 14.40. C_7H_{14}. Calculated %: C 85.62. H 14.38.

Cis-1-Methyl-3-ethylcyclobutane: b.p. 91.0-91.1°/760 mm, n_D^{20} 1.4043, d_4^{20} 0.7316, MR_D found 32.81, calculated for C_7H_{14} 32.32 (MR_D increment 0.49).

Found %: C 85.56; 85.53; H 14.27; 14.43. C_7H_{14}. Calculated %: C 85.62; H 14.38.

The aniline points of the stereoisomers of 1-methyl-3-ethylcyclobutane and 1,3-dimethylcyclobutane are given in Table 2.

TABLE 2

Hydrocarbon	Aniline point trans-	Aniline point cis-
1,3-dimethylcyclobutane	53.6	48.9
1-methyl-3-ethylcyclobutane	57.2	52.2

3. Di-(3-methylcyclobutyl) ketone

$CH_3 - CH \overset{\displaystyle CH_2}{\underset{\displaystyle CH_2}{\big<}} CH - CO - CH \overset{\displaystyle CH_2}{\underset{\displaystyle CH_2}{\big>}} CH - CH_3$
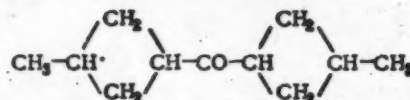
28.1 g of freshly distilled 1-methylcyclobutane-3-carboxylic acid was passed at a rate of 11.5 ml per hour at 420° through a tube containing 50 g of freshly reduced manganous oxide. After extraction with sodium carbonate solution, in order to remove unreacted acid, the neutral reaction product was distilled from a Favorsky flask, and the main fraction, boiling at 218-223°/759.5 mm, n_D^{20} 1.4586, d_4^{20} 0.9142, was collected; yield 43.5%, calculated on the amount of acid taken for the reaction. The MR_D

found was 49.65, calculated for $C_{11}H_{18}O$ 48.61, (MR_D increment 1.04, or 0.52 per cyclobutane ring).

We assumed that this fraction is a mixture of stereoisomeric di(3-methylcyclobutyl) ketones, although its carbon content is somewhat lower than expected. The semicarbazone, prepared in the usual way, and four times recrystallized from aqueous methanol, melted at 118°.

Found %: N 18.85; 18.74. $C_E H_{21}ON_3$. Calculated %: N 18.91.

The ketone did not give a crystalline product with 2,4-dinitrophenylhydrazine; the heavy orange-colored oil obtained was not analyzed.

4. Di-(3-methylcyclobutyl)-methane.

$$CH_3-CH \overset{CH_2}{\underset{CH_2}{\diagdown \diagup}} CH-CH_2-CH \overset{CH_2}{\underset{CH_2}{\diagdown \diagup}} CH-CH_3$$
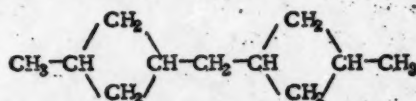
This was prepared from the above ketone, as well as from the fraction of b.p. 213-220° which is always obtained as a by-product during fractionation of the products of synthesis of 3-formyl-1-methylcyclobutane and of 3-acetyl-1-methylcyclobutane.

A solution of 33 g (0.2 mol.) of di-(3-methylcyclobutyl) ketone or of the fraction of b.p. 213-220° in 35 ml of absolute ethanol was added gradually to 22 g (0.44 mol.) of hydrazine hydrate in 25 ml of ethanol, and the mixture was heated on a water bath for four hours. The ethanol was distilled off on the following day, from an oil bath at 140°, and the residual oil was dehydrated by adding anhydrous caustic alkali. The hydrazone was decomposed as before [1], without previous distillation. The hydrocarbon so obtained was washed successively with 50% acetic acid, 50% sulfuric acid, and 10% sodium hydroxide solution, dried with calcium chloride, and distilled from metallic sodium, giving 9.2 g of a hydrocarbon of b.p. 178-184°/ 747 mm; the b.p. of this product was not changed by redistillation. Owing to the small amount of this product, it was not subjected to further fractional distillation, although it must have consisted of a mixture of stereoisomers, as was mentioned earlier in this paper. The hydrocarbon had the following properties; n_D^{20} 1.4402, d_4^{20} 0.8027, MR_D found 49.98, calculated for $C_{11}H_{20}$ 48.56. (MR_D increment 1.42, or 0.71 per cyclobutane ring).

Found %: C 86.70, 86.44; H 13.24; 13.22. $C_{11}H_{20}$. Calculated %: C 86.75; H 13.25.
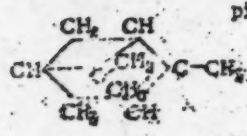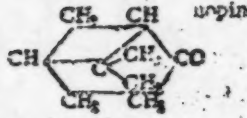
Molecular refraction of compounds possessing the cyclobutane ring.

All the cyclobutane derivatives so far prepared have a higher molecular refraction than the theoretical. Wallach [2] in 1889 found that for the sodium line D the molecular refraction of pinene and of some of its derivatives exceeded their atomic refraction by an amount of about 0.4. Oestling [3] in 1912 tabulated the molecular refractions of the 16 cyclobutane derivatives then known.

TABLE 3

Substance	Increment MR_D	Substance	Increment MR_D
1. $\overset{CH_2-CH_2}{\underset{CH_2-CH_2}{\vert \qquad \vert}}$ cyclobutane	0.21	6. $\overset{CH_2-CH_2}{\underset{CH_2-CH-COOC_2H_5}{\vert \qquad \vert}}$ ethyl cyclobutanecarboxylate	0.43
2. $\overset{CH-CH_2}{\underset{CH_2-CO}{\vert \qquad \vert}}$ cyclobutanone	0.49	7. $\overset{CH_2-CH_2}{\underset{CH_2-C(COOC_2H_5)_2}{\vert \qquad \vert}}$ diethyl cyclobutane-1,1-dicarboxylate	0.37
3. $\overset{CH_2-CH_2}{\underset{CH_2-CHOH}{\vert \qquad \vert}}$ cyclobutanol	0.42	8. $\overset{CH_2-CH-COOCH_3}{\underset{CH_2-CH-COOCH_3}{\vert \qquad \vert}}$ dimethyl cyclobutane-1,2-dicarboxylate	0.54
4. $\overset{CH_2-CH_2}{\underset{CH_2-CH-CH_2OH}{\vert \qquad \vert}}$ cyclobutylcarbinol	0.53	9. $\overset{CH_2-CH_2 \qquad CH_2-CH_2}{\underset{CH_2-CH-COO-CH-CH_2}{\vert \quad \vert \qquad \vert \quad \vert}}$ cyclobutyl cyclobutanecarboxylate	$\frac{0.84}{2} = 0.42$
5. $\overset{CH_2-CH_2}{\underset{CH_2-CH-COOH}{\vert \qquad \vert}}$ cyclobutanecarboxylic acid	0.49		

TABLE 3 - (continued)

Substance	Increment MR$_D$
10. CH_2-CH_2 CH_2-CH_2 $CH_2-CH-COO-CH_2-CH-CH_2$ cyclobutylmethyl cyclobutanecarboxylate	$\dfrac{0.96}{2} = 0.48$
11. CH_2 CH CH CH_2 $C-CH_2$ CH_2 CH_2 CH pinene	0.49
12. CH_2 CH CH CH_2 CO C CH_2 CH_2 CH_2 norpinone	0.57
13. $CH_3-CH-CH_2COOCH_2$ methyl pinate $CH-C$ CH_2 CH_2 $COO-CH_3$	0.44
14. $CH_2-CH-COOCH_3$ methyl norpinate $CH-C$ CH_2 CH_2 $COOCH_3$	0.48
15. $CH_2-CH-CH_2-CH_2OH$ glycol prepared CH_2 from ester of pinic $CH-C$ acid CH_2 CH_2OH	0.31
16. $H_3C-OOC-CH$ CH_2 CH_2 $CH-COOCH_3$ CH_2 C CH_2 methyl spiroheptanedicarboxylate	$\dfrac{1.14}{2} = 0.57$

The compounds described in this and in the preceding paper, however, show a higher increment of MR$_D$, as is evident from Table 5.

Oestling, on the basis of the data of Table 3 (with the exception of compounds Nos. 1, 7, 15 and 16), derived a value of 0.48 for the increment in molecular refraction. This value was quoted by Eisenlohr in his "Spektrochemie organischer Verbindungen" [4], and has continued to be cited in works of reference.

A consideration of the molecular refractions of cyclobutane hydrocarbons synthesized since 1912 shows that the average value of the increment is very close to Oestling's value.

TABLE 4
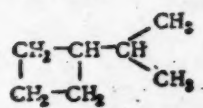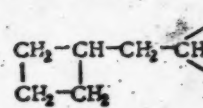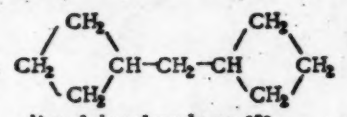
Substance	Increment MR$_D$
1. $CH_2-CH-CH_3$ methylcyclobutane [5] CH_2-CH_2	0.53
2. $CH_2-CH-C_2H_5$ ethylcyclobutane [6] CH_2-CH_2	0.45
3. $CH_2-CH-C_3H_7$ propylcyclobutane [7] CH_2-CH_2	0.51
4. $CH_2-CH-CH$ CH_3 isopropylcyclo-butane [8] CH_2-CH_2 CH_3	0.41
5. $CH_2-CH-CH_2-CH$ CH_3 isobutylcyclo-butane [9] CH_2-CH_2 CH_3	0.45
6. CH_2 CH_2 CH_2 $CH-CH_2-CH$ CH_2 CH_2 CH_2 dicyclobutylmethane [9]	0.47
Average increment of MR$_D$	0.47

The increase in the increment of molecular refraction may be ascribed to the circumstance that the cyclobutane derivatives in question are disubstituted ones, and hence represent mixtures of cis- and trans- isomers. This is shown by their indefinite boiling points, and by the fact that the last two compounds of Table 5, 1,3-dimethylcyclobutane and 1-methyl-3-ethylcyclobutane, have been separated by fractional distillation into their stereoisomers. It appeared that whereas the cis-isomers of these hydrocarbons have an increment of molecular refraction fairly close to the mean value calculated for the various monosubstituted cyclobutanes, the trans-isomers have a much higher increment, amounting for trans-1,3-dimethylcyclobutane to +0.68, and for 1-methyl-3-ethylcyclobutane to +0.64. This explains the elevated values of MR$_D$ found for the disubstituted cyclobutanes. It is, in connection with this, necessary in speaking of the increment of molecular refraction of cyclobutane derivatives to take into account their structure, and in particular the number of substituents in the ring, on which depends the possibility of the existence of stereoisomeric forms.

SUMMARY

1. The new compound 1-methyl-3-ethylcyclobutane has been synthesized and separated into its cis- and trans- isomers.

TABLE 5

	Substance		Increment MR_D
1.	$CH_2-CH-COOH$ $\;\;\;\; \| \;\;\;\;\; \|$ $CH_3-CH-CH_2$		0.58
2.	$CH_2-CH-COCH_3$ $\;\;\;\; \| \;\;\;\;\; \|$ $CH_3-CH-CH_2$	3-acetyl-1-methyl-cyclobutane	0.61
3.	$CH_2-CH-CHO$ $\;\;\;\; \| \;\;\;\;\; \|$ $CH_3-CH-CH_2$	3-formyl-1-methyl-cyclobutane	0.64
4.	$CH_2-CH-CO-CH-CH_2$ $\;\;\;\; \| \;\;\;\;\; \| \;\;\;\;\; \| \;\;\;\;\; \|$ $CH_3-CH-CH_2 \;\;\; CH_2-CH-CH_3$ di-(3-methylcyclobutyl) ketone		$\dfrac{1.04}{2} = 0.52$
5.	$CH_2-CH-CH_2-CH-CH_2$ $\;\;\;\; \| \;\;\;\;\; \| \;\;\;\;\; \| \;\;\;\;\; \|$ $CH_3-CH-CH_2 \;\;\; CH_2\;CH-CH_3$ di-(3-methylcyclobutyl)-methane		$\dfrac{1.40}{2} = 0.70$
6.	$CH_2-CH-CH_3$ $\;\;\;\; \| \;\;\;\;\; \|$ $CH_3-CH-CH_2$	1,3-dimethylcyclo-butane	0.59
7.	$CH_2-CH-C_2H_5$ $\;\;\;\; \| \;\;\;\;\; \|$ $CH_3-CH-CH_2$	1-methyl-3-ethyl-cyclobutane	0.56
	Average increment of MR_D		0.60

2. The new compound di-(3-methylcyclobutyl)-methane has been synthesized as a mixture of stereoisomers.

3. A number of new disubstituted cyclobutane derivatives have been prepared and described.

4. The disubstituted cyclobutanes are shown to have an elevated increment of molecular refraction, due to the effect of the trans-isomers.

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EFFECT OF THE DIMENSIONS OF THE ELEMENTARY CRYSTALLITES ON THE

POROSITY AND ACTIVITY OF Al$_2$O$_3$ CATALYSTS OF DEHYDRATION REACTIONS

A. M. Rubinshtein, V. E. Vasserberg, and N. A. Pribytkova

A more or less poly-disperse precipitate is obtained in any process of precipitation of hydroxides. Under standard conditions this follows during the whole duration of the process from the probable distribution of the particles, while under ordinary conditions of precipitation additional factors are the variability of physical (stirring, and the like) and chemical conditions (progressive diminution of the concentration of the cations undergoing precipitation, and increase in the concentration of other cations in the solution). We have not been able to trace any reference in the literature to the effect of the poly-dispersity of hydroxides on the structure and the properties of the oxide catalysts obtained therefrom by dehydration. We have attempted to investigate this question, taking alumina as the oxide, and separating the precipitated aluminum hydroxide into fractions by a sedimentation method. Our investigations had as their object to answer the questions: 1) Are there any differences in the activity of the Al$_2$O$_3$ obtained from the different hydroxide fractions? 2) Are there any differences in structure between the oxides produced from the different hydroxides? 3) What differences are there between the specific surfaces of the oxides prepared from different hydroxide fractions? Our studies involved the investigation not only of the catalytic properties of the oxides, but also of their X-ray structure and of their adsorbent properties. This gave us a sufficiently full picture of the properties of the specimens of Al$_2$O$_3$ as dehydration catalysts.

EXPERIMENTAL

Preparation of Specimens of Catalysts.

Our initial hydroxide was obtained by precipitation with 5% aqueous ammonia from a boiling solution of 250 g of Al(NO$_3$)$_3$, 9H$_2$O in 3 liters of water, and was washed by decantation with hot water until the reaction for the NO$_3$ ion became negative. The volume of the suspension was then made up to 3 liters, and the suspension was shaken and allowed to stand for 24 hours, after which the upper two liters, with the most highly disperse precipitate, was removed (suspension I), the volume of the residue was made up to 3 liters, and the operation was repeated, giving suspension II, and the residue was again diluted, giving further suspensions, according to the scheme given in Fig. 1. Catalyst No. 1 was prepared from the smallest particles of hydroxide from suspensions I and II, catalyst No. 2 from suspension III and IV, and catalyst No. 3 from the largest particles deposited at all stages of the process.

We originally intended to prepare the specimens separately from each suspension, but we found that we had to unite pairs of suspensions, in order to have enough material for all the determinations necessary. Attempts at determining the particle size of the various hydroxide suspensions by means of Rehbinder's sedimentometer were unsuccessful, owing to the very small rate of sedimentation of the smaller particles, and to the stopping up of the lower part of the sedimentometer tube by the gelatinous precipitate, which prevented any change in the level in the graduated part of the instrument.

All the specimens were pressed into cylinders of the same size, using a press with the same aperture, the cylinders were dried in air, and were heated at 360° under standarized conditions, to constant weight. Catalysts Nos. 1, 2, and 3 were thus prepared, in amounts of 9.2, 4.9, and 13.4 g, corresponding with 33.4, 17.8, and 48.8% of the total amount of Al$_2$O$_3$ produced. The specific weights of the heaped catalysts 1, 2 and 3 vary to some extent (see Table 6). Their residual water content was determined by heating to constant weight at 900-1000°; the results are given in Table 6.

Experimental Data

The activites of the Al$_2$O$_3$ catalysts were determined basically from their effect in the dehydration of 77.5%

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            ┌─────────────────────────────┐
            │ Hydroxide washed free of NO₃'│
            └─────────────────────────────┘
                     Shaken with 3 liters
                     of water and allowed
                     to settle for 24 hours

     ┌──────────────────┐        ┌─────────────────────┐
     │ Precipitate 1 liter │  ⟍  │ Suspension I - 2 liters │ ──→
     └──────────────────┘        └─────────────────────┘
                  Volume made up to 3
                  liters, shaken, and al-
                  lowed to stand for 24 hours

        ┌──────────────┐        ┌──────────────┐
        │ Precipitate  │  ⟍     │ Suspension II │ ──→
        └──────────────┘        └──────────────┘
                  Volume made up to 3
                  liters, shaken, and al-
                  lowed to stand for 24 hours

        ┌──────────────┐        ┌──────────────┐
        │ Precipitate  │  ⟍     │ Suspension III│ ──→
        └──────────────┘        └──────────────┘
                  Volume made up to 3
                  liters, shaken, and al-
                  lowed to stand for 24 hours

        ┌──────────────┐        ┌──────────────┐
        │ Precipitate  │  ⟍     │ Suspension IV │ ──→
        └──────────────┘        └──────────────┘
              │
        Catalyst No. 3
```
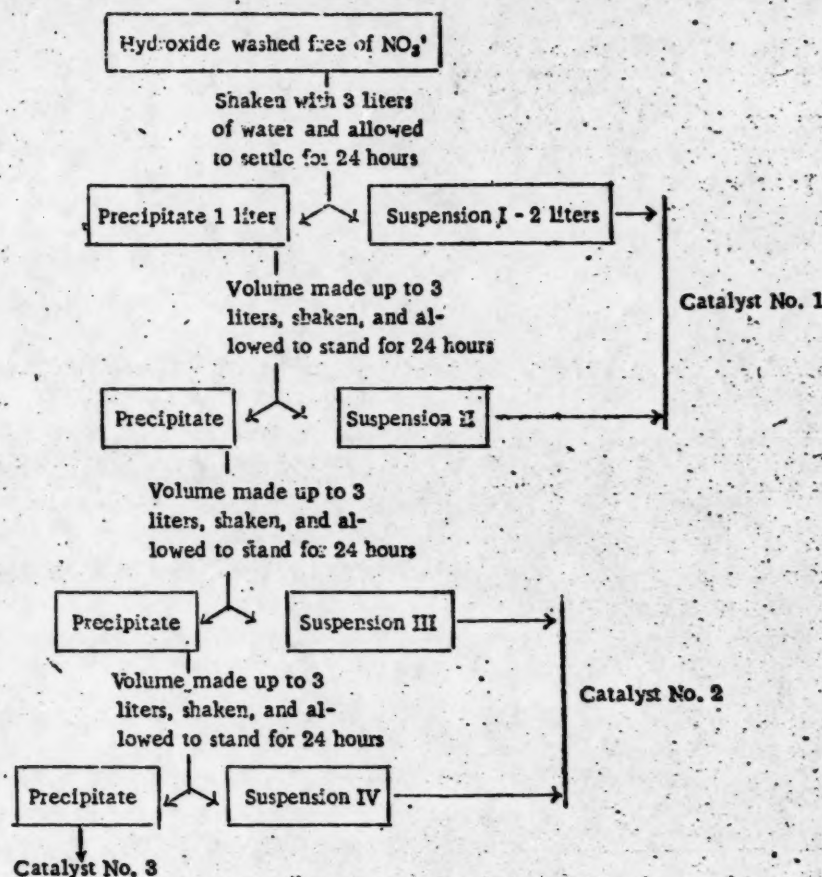
Fig. 1. Schema of preparation of catalysts

formic acid and of 96% ethanol; additional experiments were later also performed with n-butanol and n-pentanol. The experiments were performed on flowing systems, in a Vaskevich reactor [1], which is adapted to use with small amounts of catalyst. The reactor was warmed in an oven, the temperature of which was regulated by means of a contact galvanometer, the temperature of the catalyst being measured by means of a thermocouple. For all experiments 1 g (2 ml) of catalyst was taken. The rate of flow of the substrates was maintained constant at the rate of 2 liters per liter of catalyst per hour.

The results (reduced to N.T.P.) obtained in the basic experiments are given in Tables 1 and 2. They show that the relative activities of the catalysts 1, 2, and 3 as found for dehydration of HCOOH are also applicable to dehydration of ethanol. Since the amount of catalyst taken was in all cases 1 g., the data given characterize the specific activity of each of the specimens of Al_2O_3 studied. Tables 1 and 2 also give the amounts of by-products formed, viz., CO_2 and H_2 from dehydrogenation of HCOOH, and CH_4, CO_2, and H_2 from ethanol.

These results show that under the given conditions the main reaction of dehydration was complicated very little by side-reactions. We should add that the figures given in Tables 1 and 2 for amounts of by-products must be regarded as only approximate, in view of the very small volumes of gases remaining after absorption of CO_2 and CO, in the case of HCOOH, and of CO_2 and C_2H_4 in the case of ethanol. This made it necessary to dilute the residues with large amounts of nitrogen, in order to have a sufficient volume of gas for the manipulations associated with their determination.

If we take the specific activity of Catalyst No. 3 as unity, then the specific activities of catalysts Nos. 1 and 2 would be expressed by the figures 0.68 and 0.64, for HCOOH, and 0.59 and 0.49 for ethanol.

TABLE 1

Experimental Results for Decomposition of HCOOH

No. of cat- alyst	Ml of gaseous products (at N.T.P.) evolved per ml of HCOOH											
	At 275°				At 300°				At 325°			
	Σ	CO_2	CO	H_2	Σ	CO_2	CO	H_2	Σ	CO_2	CO	H_2
1	150.2	8.4	132.6	8.4	244	10.0	227.0	7.6	376.0	25.2	325.0	24.1
2	123.9	3.27	113.0	7.4	227.0	8.4	207.0	11.4	338.0	14.1	306.0	18.3
3	267.0	10.0	248.0	10.0	357.0	6.1	342.0	7.9	504.0	10.0	482.0	10.0

TABLE 2

Decomposition of Ethanol at 325°

No. of cat- alyst	Ml of product (at N.T.P.) evolved per ml of ethanol				
	Σ	C_2H_4	H_2	CO_2	CH_4
1	96.8	83.2	2.6	5.4	4.35
2	79.3	69.2	5.0	2.7	1.8
3	158.9	152.0	—	2.4	4.0

X-Ray Study of Spec- imens of Catalysts

The Debyeograms of the catalyst were taken with iron radiation ($K_\alpha = 1.932$ A) on Kodak films, with an exposure time of 6 hours, at 30 kV and 10 mA. All specimens gave crystallite X-ray diagrams, but the Roentgenogram of Catalyst No. 1 exhibited a pronounced background effect, which rendered impossible its photometric study for the determination of the dimensions of the elementary crystallites. The diagrams showed that all the catalysts consisted of γ-Al_2O_3, and that other modifications of Al_2O_3 were absent, as were also its crystalline hydrates. The relevant data are given in Table 3, from which it appears that the magnitude of the parameter for the face-centered cubic crystal lattice of γ-Al_2O_3 differs little from specimen to specimen.

The microphotometric curves taken from the Roentgenograms were recorded with the aid of a registering Siegbahn microphotometer, with a magnification of 2.5. Measurements of the half-width of the lines of Brill's curves [2] served as a basis for arriving at the values of $\eta \frac{R}{r}$, and the values of η and of λ (linear dimensions of the elementary crystallites) were then derived. The results given in Table 4 show that there is satisfactory agreement between the values of λ obtained for different angles of reflection, which testifies to the cubic form of the Al_2O_3 crystallites in the specimens examined.

TABLE 3

Roentgenostructural Data for the Catalysts
(Derived from Experimental Results)

hkl	No. 1		No. 2		No. 3	
	J	$2 \sin\theta$	J	$2 \sin\theta$	J	$2 \sin\theta$
222	medium	0.860	—		medium	0.838
004	medium	0.970	medium	0.992	strong	1.018
024	medium	1.080	—		weak	1.080
333/511	weak	1.296	medium	1.278	medium	1.294
004	strong	1.406	strong	1.390	weak	1.410
244/600	weak	1.490	—	—	weak	1.500
444	medium	1.730	—	—	medi- um/weak	1.726
$\underline{a}$ mean		7.83 A		7.82 A		7.80 A

Determination of the Specific Surface of the Catalysts

The determination of the specific surface of the catalysts was based on measurements of the adsorption isotherms for the vapors of methanol and of n-pentane at 25°, made using the ordinary apparatus, with a quartz micro-balance. The methanol and the pentane used were first subjected to thorough rectification in a laboratory column, effectiveness 30-40 theoretical plates. The
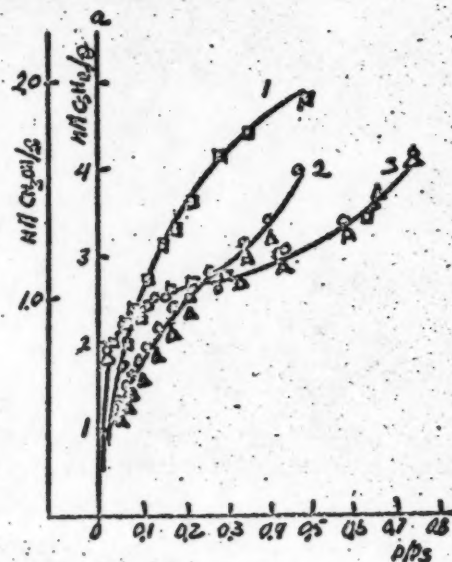

Fig. 2. Adsorption isotherm for methanol or n-pentane vapors, at 25°; 1) Catalyst No. 3, C_5H_{12}; 2) catalysts Nos. 1 and 2, C_5H_{12}; 3) catalysts Nos. 1, 2, and 3, CH_3OH.

TABLE 4

Determination of Dispersity (Size of Elementary Crystals)

No. of cat- alyst	hkl	Half- width of line, in mm	θ accord- ing to Roentgen- ogram	$\eta \frac{R}{r}$	η	λ,A	λ_{mean},A
2	004	1.44	20.7	0.285	0.00437	35.5	
	044	1.52	44.1	0.237	0.00440	35.1	35.3
3	004	0.96	30.6	0.164	0.00278	55.3	
	333	1.08	40.55	0.180	0.00305	50.5	51.4
	044	1.12	44.8	0.188	0.00318	48.3	

TABLE 5

Adsorption of Methanol and n-Pentane, in m-mole/g of Catalyst

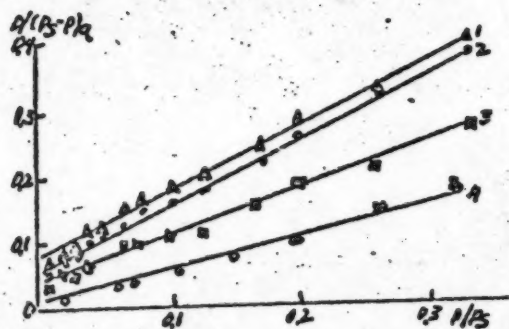|	Methanol				Pentane		
p/p_s	Catalyst No. 1	Catalyst No. 2	Catalyst No. 3	p/p_s	Catalyst No. 1	Catalyst No. 2	Catalyst No. 3
0.02	2.054	1.922	1.944	0.009	0.335	0.243	0.415
0.06	2.209	2.198	2.214	0.023	0.413	0.310	0.551
0.08	2.416	2.332	2.322	0.029	0.424	0.363	0.727
0.11	2.460	2.452	2.430	0.040	0.480	0.387	0.703
0.15	2.563	2.533	2.675	0.051	0.525	0.446	
0.20	2.511	2.545	2.700	0.064	0.614	0.497	0.791
0.27	2.598	2.640	2.820	0.084	0.673	0.582	1.014
0.31	2.736	2.760	2.682	0.104	0.766	0.660	1.103
0.42	3.000	2.891	3.060	0.128	0.870	0.766	1.280
0.43	3.124	3.000	3.116	0.172	0.960	0.854	1.350
0.57	3.331	3.316	3.186	0.210	1.038	0.943	1.446
0.63	3.581	3.693	—	0.264	1.116	1.092	1.694
0.72	4.194	4.216	—	0.328	1.265	1.207	1.774
				0.390	1.373	1.295	1.894
				0.464	1.596	1.557	1.926

Fig. 3. BET curves for Catalysts 1, 2, and 3, with methanol and with n-pentane: 1) Catalyst No. 2, C_5H_{12}; 2) Catalyst No. 1, C_5H_{12}; 3) Catalyst No. 3, C_5H_{12}; 4) Catalysts No. 1, 2, and 3, CH_3OH.

magnitude of the specific surface was calculated by the method of Brunnauer, Emmet, and Teller. The values obtained for adsorption, in m-mole/g, and the rectilinear curves derived therefrom by the equation of Brunnauer, Emmet, and Teller are shown in Figures 2 and 3 (see Table 5).

Relation Between Structure, Surface, and Activity of the Catalysts

The results reported in this paper show that the catalysts prepared from different hydroxide fractions are not identical. This is evident from a comparison of their physical properties and of other data presented in Table 6, and also from their specific activity ratios for the reactions of dehydration of HCOOH and ethanol. Thus Catalyst No. 3 is 1.5-2 times more active than Catalyst No. 1 in the reactions of dehydration of HCOOH or ethanol, at different temperatures, and Catalysts No. 1 and 2 in turn differ considerably in activity, although their specific weights differ very little, and although their specific surfaces are very similar, for both adsorbates (we were not able to establish whether the dimensions of the elementary crystallites of Catalysts 1 and 2 differed, owing to the interference of the background which prevented photometric study of the Roentgenograms of Catalyst No. 1; a visual comparison of the Roentgenograms of Catalysts 1 and 2 seemed to show that the breadth of the lines was very similar in both cases). We emphasize that the preparations of Al_2O_3 studied all had practically identical crystal lattice constants.

A comparison of the specific activity of the catalysts showed that No. 2 was the least active. This is apparently connected with its greater content of residual water, as shown by its loss of weight when heated to 900-1000°. Since the Roentgenograms show only Al_2O_3 lines (Table 3), those of γ-AlOOH being absent, it may be concluded either that the latter phase is amorphous to X-rays, in view of its low content, or, more probably, that the residual water of catalysts dried at 360° is present as an adsorbate on γ-Al_2O_3. The reciprocal relationship between the residual water content of the catalysts and their activity in both the reactions is found to be practically linear, as is shown by Figure 4.

TABLE 6

Physical constants and activity ratios of the catalysts

Cata-lyst No.	Amt. ob-tained, g	% of total amount	Heaped sp. wt.	% Weight loss when calcined	Sp. surface in sq. m. per g		Linear di-mensions of crystal-lites, in A	Relative activity in dehydration of	
					CH_3OH	$p\text{-}C_5H_{12}$		HCOOH	C_2H_5OH
1	9.2	33.4	0.575	9.9	286	182	≤ 35	0.68	0.59
2	4.9	17.8	0.566	13.04	286	179	35	0.64	0.49
3	13.4	48.8	0.542	5.42	286	264	51.4	1.00	1.00

The fall in activity as the water content rises may be due to its adsorption at the active centers of the catalysts, i.e., to blocking of these centers by water molecules, or to interference with surface diffusion of the reacting substances and of reaction products by water molecules present in the micro-pores of the catalysts.

The Roentgenographic data, which give no evidence for the presence of γ-AlOOH, lead to the explanations of the inhibiting effect of water given above, since at the temperature of the dehydration experiments γ-AlOOH gradually loses water, which may then lower the activity of the catalysts, either by blocking active centers, or by hindering diffusion.

In addition to comparing the linear dimensions of the elementary crystallites of the catalysts, and the magnitudes of their specific surfaces, we attempted to determine or compare their porosity, by the methods described by Dubinin [3] and Kiselev [4] for estimation of the pore size of adsorbents. With this object in view we measured the surfaces by the method of adsorption of the vapors of methanol and n-pentane. We selected the most trustworthy of the published values for the area occupied by a molecule of these substances, viz., 33.2 A for pentane [5], and 145 sq. m. per mM for methanol [5]. We found that the adsorption isotherms for methanol, and the values for the specific surfaces of the three catalysts hence calculated, are practically identical (Figs. 2 and 3, Table 6). The adsorption isotherms for n-pentane, and the derived specific surfaces, are, however, practically identical for catalysts 1 and 2, but are both much greater for catalyst No. 3.
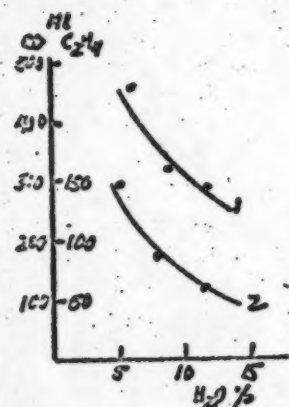
Fig. 4. 1) HCQOH; 2) C_2H_5OH

The smaller figures for adsorption of n-pentane than of methanol for catalysts 1 and 2 can be explained only on the assumption that parts of the surface of these catalysts are inaccessible to the relatively larger n-pentane molecules; such parts of the surface may be supposed to be the walls of the finest micro-pores. This explanation is in good correspondence with the conditions of preparation of the catalysts, and with the results of X-ray studies.

The differences between the values for the specific surface with regard to methanol (286 sq.m. per g for all three catalysts) and to pentane (179 and 264 sq.m. per g) can also be ascribed to differences in the size of the adsorbed molecules. Our results are in agreement with published references to differences in the values of specific surface derived from measurements of adsorption of substances whose molecules are of widely different size; thus the specific surface of a specimen of Al_2O_3 was found to be 141 or 70 sq.m. per g., according to whether the adsorbate was N_2 or $C_{17}H_{35}COOH$ [7]. Our findings show that considerable differences in specific surface, markedly affecting the activity of the catalysts, are obtained with much smaller differences between the size of the mole-

cules, as with CH_3OH and C_5H_{12}. These findings show clearly that the method for determination of the specific surface of catalysts based on measurements of low temperature adsorption of nitrogen (area occupied by a molecule is 16.2 A^2) is inacceptable, in particular for the case of organic catalysis, in which the reacting molecules are of relatively large dimensions. It is in such cases preferable to derive the measurements of specific surface from values obtained for adsorption of substances of molecule size comparable to that of the substance entering into catalyzed reaction. Similar conclusions regarding the unsuitability of relatively large molecules for measuring the actual surface of micro-pored adsorbents have been made by Kiselev et al. in a recently published paper [6].

It follows from the observation that the specific surface of the catalysts, as derived from measurements of adsorption of methanol, is the same in all cases, although their activities are different, that some complex relationship must exist between the activity of a catalyst and its specific surface. The usual assumption that differences between activity of catalysts are due to differences in the number of active centers per unit of surface, as measured by physical adsorption methods, is obviously inadequate; it is necessary also to include a consideration of porosity characteristics of the catalysts. Thus in our case the smaller surface of the more highly dispersed catalysts Nos. 1 and 2, as derived from the measurements of adsorption of n-pentane, shows that the diameter of the micro-pores of these catalysts is smaller than of catalyst No. 3, and this leads to diminution in their activity, although they have the same specific surface as catalyst 3 with regard to methanol.

The large specific surface of catalyst 3, with regard to pentane, is not fortuitous. It is obviously connected with the large linear dimensions of the Al_2O_3 crystallites of this catalyst, which when packed together to give secondary particles give rise to pores of larger diameter than do the smaller crystallites of catalysts 1 and 2. This is connected with the fact that catalyst No. 3 is prepared from the most coarse-grained and rapidly settling fraction of aluminum hydroxide. On the other hand it is well known that with considerable increase in particle size an abrupt fall in specific surface and in catalytic activity ensues. There should, therefore, exist certain limiting sizes of the elementary crystallites for which catalytic activity is at a maximum. An optimum dispersity was found to exist for a number of catalysts [8], and for various reactions [9]. As appears from the present paper, one of the most important factors, of a purely structural nature, responsible for the existence of an optimum value for dispersity, is the most favorable diameter of the micro-pores for a given reaction; these micro-pores are in turn formed by crystallites of certain optimum dimensions which are aggregated to give the secondary particles (catalyst granules).

When the dimensions of the elementary crystallites are very small, the micro-pores, which are the crevices between crystallites which have adhered to each other at certain angles, may be too small to permit of the entry of the reacting molecules. This explains why the maximum activity does not coincide with the greatest dispersity, as measured Roentgenographically. The optimum dispersity is that at which the dimensions of the elementary crystallites are such as to lead to the formation of micro-pores of a diameter similar to or greater than that of the reacting molecules. It is obvious that with further increase in the dimensions of the elementary crystallites, and hence in the diameter of the pores, the latter may assume the nature of transport pores, in view of their large size; an inevitable consequence of this process would be a considerable fall in the specific surface, and in the catalytic activity.

We thus have an explanation of the fall in catalytic activity as the dimensions of the elementary crystallites deviate from the optimum. It is evident that the change in activity observed as the dispersity differs from the optimum, in either direction, should proceed smoothly, as has been found experimentally [8].

The dependence of the micro-pore diameters on the dimensions of the elementary crystallites of which the secondary particles are built up may readily be represented schematically, taking the shape of the elementary crystallites as being approximately spherical. This has been done in Fig.5, which shows that the diameter of the pores increases with the diameter of the spheres. The actual crystallites are not, of course, spherical — they are polyhedral bodies. This does not, however, affect the general nature of the process; for an identical statistically most probable mutual orientation of crystallites of a given shape packed in a secondary particle the dimensions of the pores will be found to be greater for crystallites of greater linear dimensions. Bearing in mind that the magnitude of the specific surface is basically determined by the dimensions of the micro-pores, the role of the dimensions of the elementary (primary) particles becomes obvious, as a factor determining the magnitude of the surface.

A similar explanation of the existence of an optimum of dispersity, based on purely structural considerations, is supported by the results found [10] for the dehydrogenation of HCOOH, iso-$C_5H_{11}OH$, and C_6H_{12} at nickel catalysts. Over a relatively narrow interval of optimum dispersity (20-25 Å) of nickel, the activity of the catalyst in these three reactions is not identical, especially if we take into account differences in the temperatures of the reactions. It appears that the activity at optimum dispersity of the catalyst also depends, for a given type of reaction (in this case, of dehydrogenation), on the size of the reacting molecules.

We are not inclined to consider that the structural factor described by us (dependence of size of micro-pores on the dimensions of the elementary crystallites of which the secondary particles are made up) is the sole factor determining the dispersity optimum, but we believe that it plays at least as important a role as does

chemical supersaturation [11] or capture of micro-constituents, which passes through a maximum for a given size of crystallites.
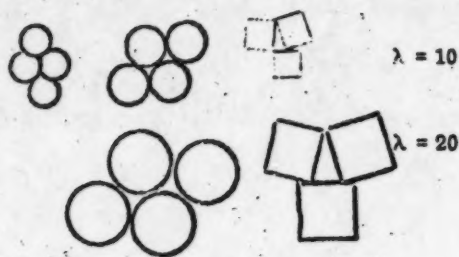

Fig. 5

This second explanation is confirmed by the very interesting results obtained by Fricke and Diefel [12] for adsorption by alumina of KH_2PO_4 from its aqueous solutions. These authors found that the ratio of adsorbed $K^{\cdot}$ to HPO_4'' varies according to the size of the Al_2O_3 particles; the ratio K/HPO_4 increases with increase in particle size. It seems to us that this effect may be connected with differences in the size of the pores of the specimens of Al_2O_3 prepared by these authors by dehydration of γ-AlOOH at different temperatures (300°, 500°, 600°, and 800°) and differences between the size of K and HPO_4 ions in the solution.

Additional experiments were performed on the dehydration of n-butanol and n-pentanol at catalysts No.1 and 3 (Table 7), in order to verify the suppositions made by us that there is a correlation between the size of the micro-pores and the dimensions of the elementary crystallites, on the one hand, and the activity of the catalyst, on the other. The results given in Table 7 (ml of reaction products per ml of alcohol under the same conditions as for the dehydration of ethanol) are those found for n-butanol.

The specific activity of the catalysts is about 10% lower than for dehydration of ethanol, but the ratio of activities of the two catalysts is about the same as before; this finding is in complete agreement with our hypotheses. The chief difference is that the dehydrogenation reaction is more in evidence in the case of n-butanol.

Experiments conducted under similar conditions with n-pentanol showed that practically no gaseous dehydration products were obtained with catalyst No.1; catalyst No. 3 showed a small activity, which fell to zero after a few minutes. Both catalysts were blackened by soot formed from the n-pentanol. Catalyst No. 3 was slightly more active at 400° (35 ml of C_5H_{10} per ml of alcohol) than at 325°. Passage of n-butanol immediately after n-pentanol has been passed shows that dehydration of the former alcohol proceeds at a satisfactory speed (90 ml of C_4H_8 per ml of butanol), showing that the catalyst has retained its activity towards butanol, in spite of its surface being covered with soot formed from the pentanol previously passed over it. These experiments show that the difference in the action of the catalysts on these two alcohols depends on the dimensions of their molecules, and is connected with the size of the pores of the catalyst. The smaller molecule of butanol penetrates into the pores, whereas the pentanol molecule reacts only with the external, geometrical surface of the catalyst, the negligible dimensions of which determine the very low activity of the catalyst in the reaction of dehydration of pentanol. Our findings show that the catalysts have a very large surface and very fine pores, and that a large proportion of the pores do not admit the larger molecules, as the mol. wt. rises, from ethanol to pentanol. It follows further from the smaller activity of catalysts No. 1 and 2 than of 3 for dehydration of ethanol that some of the micro-pores do not admit even these relatively small molecules. A sharply defined activity threshold, corresponding with a Gaussian distribution of pore diameters, occurs for n-pentanol, whereas ethanol and n-butanol molecules correspond with the middle part of the curve.

TABLE 7

Catalyst No.	Total volume of gaseous products, in ml	Volume of products in ml			
		C_4H_8	H_2	CO	CO_2
1	80.1	70.0	4.5	2.4	2.5
3	162.8	139.0	11.7	4.4	1.7

It is known that dehydration of higher alcohols takes place quite satisfactorily at a number of Al_2O_3 preparations (in particular from bauxites). This in no way conflicts with our findings, since it only shows that these catalysts possess micro-pores of large diameter.

Our experiments also confirm that such methods should be used for measuring the surface of catalysts as apply not to the total surface (from nitrogen adsorption) but to the effective active surface, i.e., to that part of the surface which is accessible to the given substrate molecules, but not to the surface of the micro-pores to which the reacting molecules have no access.

SUMMARY

A study of dehydration of HCOOH, ethanol, n-butanol, and n-pentanol at Al_2O_3 catalysts prepared from sedimentation fractions of hydroxide leads to the following conclusions:

1. The activity of catalysts prepared from different hydroxide fractions varies, the most active being catalyst No. 3, obtained from the most coarse-grained hydroxide fraction.

2. X-Ray structural analysis shows that the catalysts are all crystalline, consisting of γ-Al_2O_3 with uniform lattice constants, and not containing any other forms of Al_2O_3 or of its crystal hydrates; their residual water content appears to be in the adsorbed state. The linear dimensions of the crystallites of γ-Al_2O_3 are greatest (51-52 Å) for catalyst No. 3, and smallest ($\leqslant$ 35 Å) for catalyst No. 1, prepared from the most highly disperse hydroxide fraction.

3. The derivation of the specific surface from measurements of adsorption of methanol is unsatisfactory, inasmuch as identical values (286 sq.m. per g) were obtained for all three specimens of γ-Al_2O_3, whereas data for adsorption of n-pentane show that they have different surfaces. Catalyst No. 3, the grains of which are made up of the largest crystallites of γ-Al_2O_3 (51 A), has a specific surface of 264 sq. m. per g, as derived from n-pentane adsorption, whereas catalysts No. 1 and 2, which are made up of smaller crystallites, have a specific surface of 182 and 179 sq. m. per g., respectively.

4. It follows from the findings that (a) a catalyst, the grains of which are made up of larger particles, has a bigger surface and a greater activity than one made up of smaller particles, and (b) the specific surface derived from adsorption of smaller molecules (methanol) is greater than with larger molecules of n-pentane, that:

(I) The dimensions of the micro-pores of the catalysts are determined by the size of the elementary crystallites and by the way in which they are packed to give secondary particles (catalyst grains). The optimum dimensions of the crystallites are those which when aggregated into secondary particles giver pore dimensions commensurate with the size of the reacting molecules. A scheme is advanced, explaining the effect of this structural factor, and also the existence of an optimum of dispersity.

(II) The estimation of the specific surface of catalysts of organic reactions from low temperature adsorption of nitrogen molecules is unsatisfactory, in view of their small size, and cannot serve as a criterion of the relative activity of different catalysts.

5. The hypotheses advanced in paragraph 4 have been confirmed experimentally, for the cases of dehydration of substances having molecules of widely different size (HCOOH, ethanol, n-butanol, n-pentanol).

6. The concept of effective specific surface has been introduced, in connection with the above findings.

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OPTICAL ACTIVITY OF CELLULOSE TRIACETATE

N. M. Bazhenov and M. V. Volkenshtein

Intramolecular interferometry — a study of optical activity — is one of the most valuable methods available to us for the study of intramolecular changes and reactions. The profound ideas of the theory of the structure of organic compounds and of the mutual effects exerted by their constituent atoms, formulated by Butlerov and Markovnikov, were successfully developed by Chugaev, who applied the study of optical activity to the analysis of intramolecular reactions in complex organic substances [1]. The present paper deals with the application of the effect of temperature on optical activity to the study of internal rotations in cellulose triacetate and in simpler compounds of analogous structure.

Internal rotation about single bonds in molecules leads to a change in their configuration. The magnitude of the optical rotating power is directly dependent on the geometrical distribution of atoms in the molecule. If the molecule has a low degree of symmetry (axes of symmetry not more than the second order) the possibility of internal rotations leads to the phenomenon of rotational isomerism [2]. Change in temperature leads to change in the relative amounts of the rotational isomers in the mixture, the equilibrium constant of which is thus modified.

Since each rotational isomer of an asymmetric molecule possesses a characteristic optical activity, the value found for the latter should vary with temperature. Differences in the energy of rotational isomers may be derived from the temperature coefficients of optical activity [3]. Only a very few researches on this subject have so far been published, such as on the esters of tartaric acid [4] and on sec-butanol [5].

The more important properties of linear polymers are connected with processes of internal rotation. According to the concepts developed by us linear polymers should be regarded as equilibrium mixtures of rotational isomers [6]. We unfortunately know of no optically active, flexible, rubber-like polymers. The present paper is devoted to a polarimetric study of internal rotation in the highly optically active polymer cellulose triacetate. This has the structure:
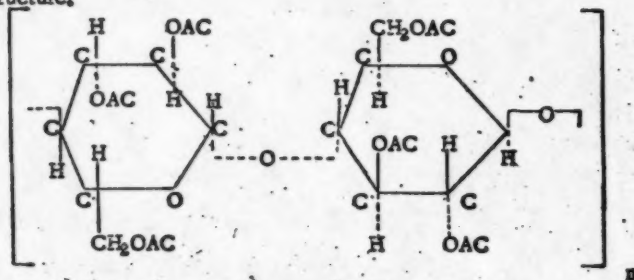
The properties of the chain as a whole are determined by the rotations relatively to each other of its component links, rotations around C–O bonds linking six-membered rings. Rotations around single bonds in the acetyl side groups are also possible. In order to study separately the effect of these and of other rotations on optical activity, research was done on an analog of a single link of the chain, α-penta-acetyl-d-glucose:
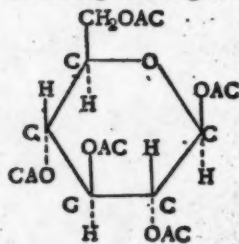
and of the analog of the pair of links, α-octa-acetyl-cellobiose:
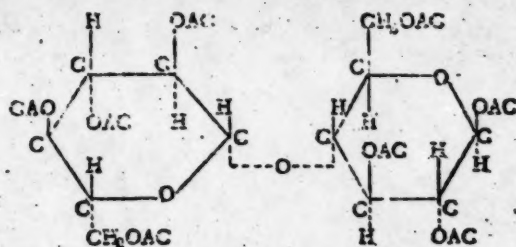
In the former case rotation is possible only in the side-chains, while in the latter rotation is additionally possible around the C—O bond joining the rings.

The greatest difficulty of the research consists in eliminating intermolecular reactions, which would also complicate the effects of temperature on optical rotation. The following relation is derived, on theoretical grounds, between the value of optical rotation and the properties of the solution [7]:

$$\Omega = \frac{[a]}{n^2 + 2} = \Omega_0 + B\frac{\epsilon - 1}{\epsilon + 2},\tag{1}$$

where [a] is the specific rotation, n is the refractive index, ε is the dielectric constant, and Ω and B are constants; Ω and Ω_0 are termed "rotivity".

Since n and ε depend on temperature, it follows that Ω must also be a function of temperature T. The functional dependence of molecular rotivity Ω, which represents optical rotatory power in absence of solvent factors, can be considered in isolation if the value of the constant B, and the dependence of n and ε on temperature, are known; this involves studies of substances in solvents of widely different n and ε.

Formula (1) is not applicable to solutions in which association may take place. We selected triacetyl-cellulose for our study, since the cellulose is practically completely esterfied, as a result of which association due to formation of hydrogen bridges arising from hydroxyl groups is excluded.

EXPERIMENTAL

The following measurements were made, in order to determine the dependence on temperature of [a], n and ε in solutions of the above-mentioned substances:

1. Rotation of the plane of polarization was measured by means of a polarimeter, set up as shown in Fig.1. Readings were taken with three wave lengths, 435, 589, and 656 mμ. The source of light was an electric glow-lamp (12V and 50W), the light from which was split up into a spectrum by means of a monochromator UM-2. The temperature range was from −10° (in some cases, from −40°) to temperatures close to those of the boiling point of the solvents. Temperatures were regulated in an ultrathermostat, not varying by more than 0.1° during the period of the measurement. The accuracy of measurement of the angle of rotation of the plane of polarized light was +0.02°. The length of the polarimeter tube was 20 cm. Even flow of the thermostat liquid (water and methanol) over the tube was assured. Dimming of the end pieces of the tubes at low temperatures was prevented by fitting protective caps with warmed windows, passing dry air through the caps.

2. At the same time, in order to take into account thermal expansion of the solution, its density was measured by means of a cathetometer, with an accuracy of up to the fourth place.

3. In order to determine rotivity

$$\Omega = \frac{[a]}{n^2 + 2}$$

it is necessary to measure the refractive index at the same temperatures and wave lengths. These measurements were conducted with an IRF-23 refractometer, with an accuracy of $\pm 2 \cdot 10^{-4}$.

4. Measurement of the dielectric constant ε and of its temperature coefficient were made with the aid of the Q-meter KV-1, at a frequency of 11 megacycles. The measuring condenser, shown schematically in Fig.2, is connected, together with the thermometer, directly to the efferent terminals of the Q-meter, thus greatly lowering the effect of scattered capacity. The temperature of all the instruments was maintained by means of
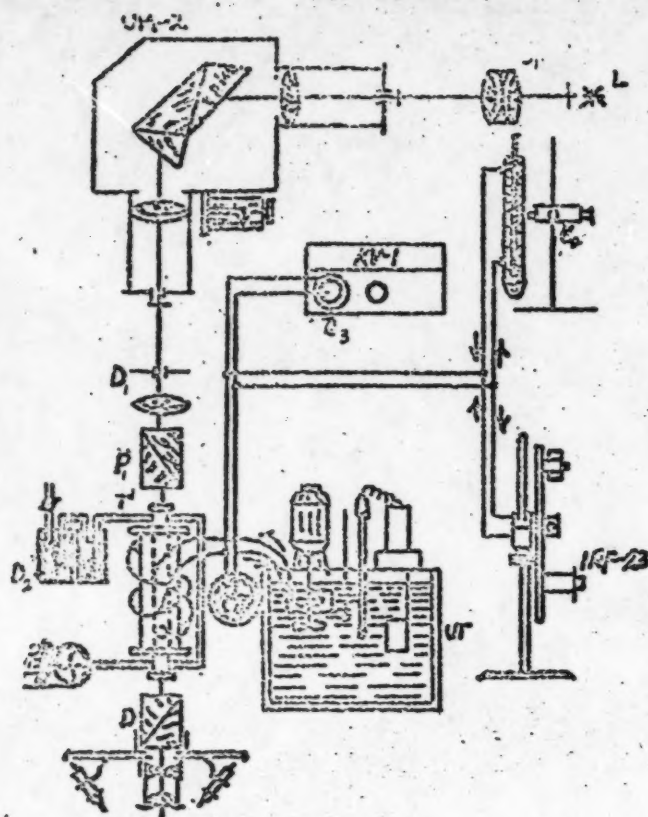
Fig. 1. Polarimeter scheme: UM-2) monochromator; C₁) condenser; L) lamp; D) diaphragm; P₁) two-field polarizer; D₁) drier; T) tube; P₂) pump; A) analyzer; UT) ultrathermostat; C₂) cathetometer; KV-1) Q-meter; C₃) condenser; IRF-23) refractometer; CA) coll' accumulator.

one and the same ultrathermostat.

Triacetylcellulose with an equivalent acetic acid content of 62.5% was purified by precipitation with ethanol from filtered solutions in the appropriate solvent. The concentration varied according to the solvent, from 0.01 to 0.05 g per ml of solvent; experiment showed that specific rotation [a] does not depend on concentration within these limits.

a-Penta-acetylglucose was prepared in our laboratory by scientific worker Sogomonyants by acetylation of glucose, by the standard method [8]. It melted at 110-111° (published m.p. 110-113°; $[a]_D^{20}$ 101.6°, in chloroform). a-Octa-acetylcellobiose was also prepared by Sogomonyants, by a standard method [9], m.p. 224-225° (published m.p. 225-226°; $[a]_D^{20}$ 42.5°, in chloroform).

Fig. 2. Measuring condenser.

Expression (1) gives a linear relation between the Ω of a substance and the value of $(\epsilon-1)/(\epsilon+2)$, at a given temperature. The values of Ω obtained by us give a certain scatter about the straight line expected for the $\Omega-(\epsilon-1)/(\epsilon+2)$ curve; this is not unnatural, if we take into account the simplifying assumptions made in the derivation of the initial formula (cf. [7]). Our case is one of a solution of a polar substance in polar solvents. We can, nevertheless, consider the curve $\Omega-(\epsilon-1)/(\epsilon+2)$ to be roughly rectilinear, and we may make use of it to determine the values of the constants B and Ω_0. We applied the method of smallest squares for selection of the most probable curve. We thus arrived at the values of Ω_0 and B, as functions of temperature. The values of Ω_0 (T) found experimentally, and calculated are given in Table 4.

DISCUSSION OF RESULTS

All three substances exhibit a noticeable dependence of real specific rotivity Ω_0 on temperature, which cannot be referred to the action of the solvent; this is evidence of the presence of internal rotations in these substances. In order to determine the nature of these internal rotations it is necessary to compare the temperature dependence of rotivity of triacetylcellulose with those of the monomer and dimer. The following possibilities may exist:

335

TABLE 1

Optical Activity of α penta-Acetyl d-glucose

Solvent	Temp. °C	Ω at wave lengths in mμ			$\frac{\epsilon-1}{\epsilon+2}$
		435	589	656	
Benzene	-10	40.77	23.04	17.51	0.312
	0	40.91	23.11	17.57	0.307
	20	41.10	23.28	17.69	0.301
	50	41.62	23.52	17.86	0.291
Dioxan	-10	31.40	24.66	19.56	0.328
	0	31.52	24.48	19.63	0.317
	20	31.72	24.33	19.75	0.299
	50	32.70	25.50	20.89	0.284
Dichloroethane	-10	49.24	25.71	20.18	0.793
	0	49.66	25.87	20.40	0.781
	20	50.02	26.18	20.77	0.757
	50	50.79	26.70	21.44	0.720
	70	51.15	26.90	21.84	0.694
Tetrachloroethane	-10	49.20	25.85	20.48	0.728
	0	49.35	25.98	20.54	0.715
	20	49.87	26.31	20.79	0.686
	50	50.32	26.60	21.12	0.634
	70	50.63	27.05	21.38	0.603
Acetic anhydride	-10	55.23	30.10	23.43	0.894
	0	55.38	30.30	23.49	0.881
	20	55.67	30.40	23.64	0.873
	50	56.14	30.80	23.83	0.860
	70	56.46	30.90	23.99	0.850

TABLE 2

Optical Properties of α octa-Acetylcellobiose

Solvent	Temp. °C	Ω at wave lengths in mμ			$\frac{\epsilon-1}{\epsilon+2}$
		435	589	656	
Methylenechloride	-10	21.99	12.18	9.41	0.753
	0	22.17	12.28	9.54	0.740
	20	22.56	12.46	9.77	0.716
	40	22.91	12.55	9.97	0.693
Dichloroethane	-10	22.83	12.30	9.75	0.793
	0	22.83	12.29	9.74	0.781
	20	22.92	12.33	9.75	0.757
	50	23.06	12.36	9.73	0.720
	70	23.15	12.39	9.72	0.694
Tetrachloroethane	-10	18.28	10.03	8.00	0.728
	0	18.29	10.02	7.98	0.715
	20	18.35	10.06	8.01	0.686
	50	18.40	10.07	7.97	0.634
	70	18.44	10.09	7.95	0.603
Dioxan	-10	18.61	9.10	7.21	0.328
	0	18.79	9.22	7.33	0.317
	20	19.15	9.50	7.60	0.299
	50	19.69	9.86	7.96	0.284
	70	20.06	10.12	8.23	0.281
Chloroform	-10	21.54	11.52	10.61	0.610
	0	21.33	11.28	10.45	0.581
	20	20.91	10.84	10.09	0.550
	50	20.32	10.03	9.56	0.515

TABLE 3

Optical Properties of Triacetylcellulose

Solvent	Temp. °C	Ω at wave lengths in mμ			$\frac{\epsilon-1}{\epsilon+2}$
		435	589	656	
Nitromethane	-10	-3.00	+0.68	+1.27	0.931
	0	-3.39	+0.33	+0.92	0.926
	20	-4.23	-0.41	+0.26	0.917
	50	-5.40	-1.55	-0.72	0.909
	70	-6.20	-2.29	-1.41	0.896
Tetrachloroethane	-10	-7.11	-2.87	-2.12	0.728
	0	-7.46	-3.21	-2.36	0.715
	20	-8.18	-3.84	-2.95	0.686
	50	-9.20	-4.79	-3.74	0.634
	70	-10.00	-5.31	-4.25	0.603
Chloroform	-10	-9.40	-4.93	-3.73	0.610
	0	-9.63	-5.15	-3.79	0.581
	20	-10.00	-5.50	-4.11	0.550
	50	-10.50	-6.03	-4.61	0.515

TABLE 4

Comparison of the Values of $\Omega_0(T)$, Obtained Experimentally and Calculated

Substance	Temp. °C	λ = 435 mμ		λ = 589 mμ		λ = 656 mμ	
		Ω_0	$\Omega_{calc.}$	Ω_0	$\Omega_{calc.}$	Ω_0	$\Omega_{calc.}$
α-Penta- acetyl- glucose	-10	22.59	22.20	18.76	18.65	14.49	14.50
	0	22.95	22.95	18.85	18.95	14.71	14.68
	20	23.74	24.20	19.45	19.45	15.07	15.08
	50	25.42	25.70	20.01	20.01	15.44	15.44
	70	27.17	26.45	—	20.28	—	15.52
α-Octa- acetyl- cello- biose	-10	8.23	8.20	3.38	3.44	0.72	0.60
	0	8.41	8.41	3.83	3.91	1.11	1.38
	20	8.77	8.75	4.87	4.65	2.55	2.55
	50	9.12	9.08	5.31	5.38	3.67	3.67
	70	—	9.22	—	5.70	—	4.15
Tri- acetyl- cellu- lose	-10	-21.52	-21.35	-15.52	-15.18	-13.34	-13.00
	0	-20.33	-20.42	-14.54	-14.45	-12.01	-12.28
	20	-18.83	-18.95	-13.25	-13.27	-10.94	-11.12
	50	-17.44	-17.47	-12.00	-12.06	-9.96	-9.97
	70	-16.81	-16.81	-11.49	-11.52	-9.49	-9.46

(a) The $\Omega(T)$ curve for triacetylcellulose is characterized by parameters which differ radically from those characterizing the corresponding curves for the monomer and dimer. In that case, the difference may be ascribed to rotations of individual links of the chain; in this case the $\Omega(T)$ curves for the dimer and the monomer should be radically different.

(b) All three $\Omega(T)$ curves have parameters which differ little from each other. In this case the effect of temperature is confined to rotation of the side acetyl groups, since there can be no question of rotation of the ring.

We attempted to describe all three curves by means of an empirical equation of the type

$$\Omega(T) = \frac{\Omega^{(1)} + \Omega^{(2)} Ae^{-\frac{E}{RT}}}{1 + Ae^{-\frac{E}{RT}}},\tag{2}$$

where $\Omega^{(1)}$, $\Omega^{(2)}$, A and E are constants, determined experimentally, R is the gas constant, and T is absolute temperature. The constants $\Omega^{(1)}$, $\Omega^{(2)}$, A and E are determined in the following way. Let

$$x_1 = \frac{E}{RT_1},$$

then

$$\Omega_1 = \frac{\Omega^{(1)} + \Omega^{(2)} Ae^{x_1}}{1 + Ae^{x_1}}\tag{3}$$

Taking $\Omega^{(1)}(x_i)$ equations for four temperatures, and eliminating $\Omega^{(1)}$ and $\Omega^{(2)}$, we obtain two expressions for A:

$$A = \frac{(\Omega_1 - \Omega_2)(e^{x_2} - e^{x_3}) - (\Omega_2 - \Omega_3)(e^{x_1} - e^{x_2})}{(\Omega_2 e^{x_2} - \Omega_1 e^{x_1})(e^{x_2} - e^{x_3}) - (\Omega_3 e^{x_3} - \Omega_2 e^{x_2})(e^{x_1} - e^{x_2})}$$

and

$$A = \frac{(\Omega_2 - \Omega_3)(e^{x_3} - e^{x_4}) - (\Omega_3 - \Omega_4)(e^{x_2} - e^{x_3})}{(\Omega_3 e^{x_3} - \Omega_2 e^{x_2})(e^{x_3} - e^{x_4}) - (\Omega_4 e^{x_4} - \Omega_3 e^{x_3})(e^{x_2} - e^{x_3})}$$

We find graphically at which values of E these equations give the same value of A. We find $\Omega^{(1)}$ and $\Omega^{(2)}$ by a reverse substitution. The results so obtained are given in Table 5 (compare with Table 4). A comparison of experimental and calculated values of Ω for $\lambda = 589$ mμ is given in Figure 3.

Agreement of the same order is obtained using other wave lengths.

Thus the temperature dependence of Ω differs little for the three substances studied. The important constant E has practically the same value in all three cases. It is of interest that the value of the constant A for triacetylcellulose is intermediate between the values for penta-acetylglucose and octa-acetylcellobiose.

Equation (2) is an empirical one, but it has a definite physical significance. Let us imagine an equilibrium mixture of two rotational isomers 1 and 2, with rotivities $\Omega^{(1)}$ and $\Omega^{(2)}$. The rotivity of the mixture is given by

$$\Omega = \frac{1}{N}\left(N_1 \Omega^{(1)} + N_2 \Omega^{(2)}\right),\tag{4}$$

where $N = N_1 + N_2$, and is the total number of molecules per unit volume, N_1 and N_2 being the number of molecules of isomers 1 and 2, respectively. The ratio $N_1 : N_2$ is determined by the difference in the energies E of the isomers

$$\frac{N_2}{N_1} = Ae^{-\frac{E}{RT}},\tag{5}$$

where A is the ratio of statistical weights of isomers 2 and 1.

TABLE 5

Parameters Characterizing Rotivity of the Substances Studied

λ in mμ	E cal/mol.	A	$\Omega^{(1)}$	$\Omega^{(2)}$
Triacetylcellulose				
435	2800	445	−37.06	−14.11
589	3000	500	−24.79	−9.42
656	3000	591	−23.74	−7.55
Mean	2900	512	−	−
α-Octa-acetylcellobiose				
435	3200	836	5.30	9.72
589	3200	814	−2.80	6.80
656	2800	722	−18.43	6.00
Mean	3100	791	−	−
α-Penta-acetylglucose				
435	3000	300	14.80	29.60
589	2800	234	15.37	21.52
656	2800	336	11.49	16.34
Mean	2900	290	−	−

Substituting in equations (5) and (4) we obtain Equation (2).

The number of different rotational isomers of our substances must in practice be very great indeed, in view of the large number of groups capable of rotation present in the molecule, and for this reason our empirical equation has no direct theoretical significance. This is also indicated by the large values of $\underline{A}$, as in reality the ratios of the statistical weights of the rotational isomers should be hundreds of times smaller. The values of $\underline{E}$ determined by us do, however, have a physical meaning, if only for giving the order of magnitude characteristic of the mean differences in the energies of rotational isomers. The usual value for the energy of rotation around single bonds is 3 kcal; this is the value of the potential barrier in the case of ethane.

We have thus found that internal rotations of the same type take place in all three substances — monomer, dimer, and polymer. These must obviously be rotations of the acetyl side chains; we were not able to find evidence for rotation of the rings relatively to each other, and this is in accordance with the known rigidity of the cellulose chain.

It is known that a certain freedom of rotation of side-chains of polymers is indicated by their specific electrical properties [10], and in other ways. Our findings show that the study of the dependence of optical activity on temperature provides a new and valuable method of investigating these important processes.

We express our sincere gratitude to Zh. S. Sogomonyants, a scientific worker of our laboratory, for preparing and purifying the substances and solutions used in our research.
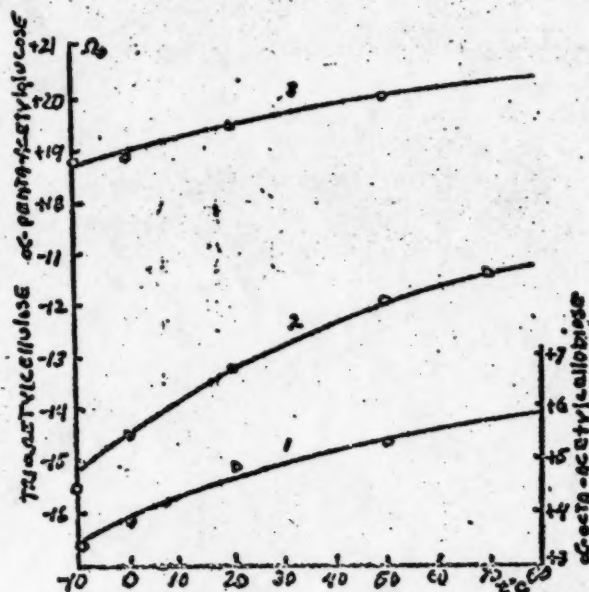

Fig. 3. Curves connecting rotivity with temperature for α-octa-acetylcellobiose, triacetylcellulose, and α-penta-acetylglucose. 1) ΔE = 2800 cal/mol.; A = 234; $\Omega^{(1)}$ = = 15.37; $\Omega^{(2)}$ =21.52;2) ΔE = 3000 cal/mol.; A = 500; $\Omega^{(1)}$ =−24.79; $\Omega^{(2)}$ =−9.42; 3) ΔE = 2800 cal/mol.; A = 234; $\Omega^{(1)}$ = 15.37; $\Omega^{(2)}$ =21.52. The curves satisfy the equation

$$\Omega_\theta = \frac{\Omega^{(1)} + \Omega^{(2)} Ae^{-\frac{\Delta E}{RT}}}{1 + Ae^{-\frac{\Delta E}{RT}}}.$$ The small

circles represent experimental values of Ω_θ.

SUMMARY

The dependence of optical activity on temperature has been studied for triacetylcellulose, α-penta-acetylglucose, and α-octa-acetylcellobiose, in various solvents, and over a wide range of temperatures and wave lengths. It was found that in all three cases internal rotation of the acetyl side-chains of the molecules took place, but that rotation relative to each other of the constituent rings of the chains did not take place.

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REACTIONS OF DIENE HYDROCARBONS WITH NITROSO-COMPOUNDS. ADDITION OF BUTA-1,3-DIENE TO NITROSOBENZENE

PART 1.

Yu. A. Arbuzov

Nesmeyanov and Ioffe in 1941 isolated from the dark brown tarry product of reaction of p-nitrosodimethyl-aniline with buta-1,3-diene a small amount of a golden yellow crystalline substance, $C_{12}H_{14}N_2$, m.p. 138-139°, by the method of chromatographic adsorption. In 1945 Nesmeyanov and Khrulev found that nitrosobenzene and buta-1,3-diene, at or slightly above room temperature, give a colorless crystalline product, m.p. 49.5-50°, in good yield. Elementary analysis of this product gives the formulas, $C_{10}H_9ON$ or $C_{10}H_{11}ON$.

I have found that buta-1,3-diene reacts smoothly with nitrosobenzene at 0°, giving a product, $C_{10}H_{11}ON$, m.p. 50-51°. The reaction thus consists in addition of 1 mol of buta-1,3-diene to 1 mol of nitrosobenzene. In my first experiments nitrosobenzene was left in a sealed tube with excess of butadiene for a number of days at 5-10°, until the reaction was completed, when the tubes were opened, excess butadiene was evaporated off, and the residue was recrystallized from light petroleum, and then from ethanol; yield of product of m.p. 50-51°– 60% of theoretical. When this same reaction was repeated on a larger scale, however, taking 32.1 g of nitro-sobenzene, the temperature of the reaction mixture rose, until the reaction ended in a violent explosion; for this reason, later experiments were conducted with cooling by means of ice. The reagents were kept in a sealed tube in an ice bath for a week, the tube was opened, excess of butadiene was evaporated off, and the residue was steam-distilled, giving a 90% yield of addition product. Subsequent experiments were conducted at 0°, diluting the reagents with various solvents (ethanol, ether, chloroform). Butadiene was added to solutions of nitrosobenzene in the solvents at 0°, the flask was left in the ice bath for 1-2 days, the solvent was distilled off, and the residue was distilled in vacuum; the yield of addition product was 90-95 %.

The addition product is readily soluble in warm light petroleum, cyclohexane, methanol, and ethanol, and in cold chloroform and acetic acid; it is practically insoluble in water. It can be steam-distilled or vacuum distilled (b.p. 107-108°/3.5 mm) without decomposition. It is hydrolyzed when heated with dilute mineral acids (10% sulfuric or 5% hydrochloric acid).

We could, on theoretical grounds, envisage two ways in which addition could take place. If the reaction proceeds as a diene synthesis the product should be 2-phenyl-3,6-dihydro-ortho-oxazine (I):
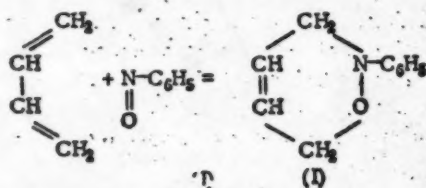
If butadiene adds on at the 1,4 positions to the nitrosobenzene nitrogen atom the product should be the N-oxide of 1-phenyl-2,5-dihydropyrrole (Ia):
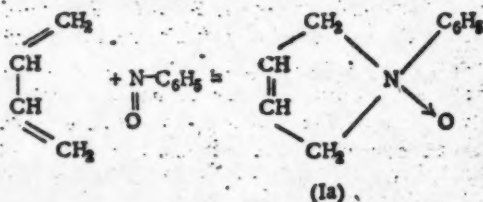

We know that sulfur dioxide reacts similarly with dienes.

The physical properties of the addition product (insolubility in water, solubility in hydrocarbons, volatility in steam, etc.) are not compatible with structure (Ia). The remaining alternative is therefore that the reaction of butadiene with nitrosobenzene proceeds according to the diene synthesis, and that the product must be 2-phenyl-3,6-dihydro-ortho-oxazine (I). An examination of the structure of the addition product confirmed this supposition.

Structure (I) for the addition product was established in the following way. Reduction of the addition product with zinc dust and acetic acid gave 4-anilinobut-2-en-1-ol (II), identified as the dibenzoyl derivative (VII) (m.p. 90-91°). Acetylation of 4-anilino-but-2-en-1-ol (II) with acetic anhydride gave the diacetyl derivative (III), oxidation of which with potassium permanganate in acetone gave N-acetyl-N-phenylglycine (IV).

The catalytic hydrogenation of 2-phenyl-3,6-dihydro-ortho-oxazine and 4-anilinobut-2-en-1-ol was next studied.
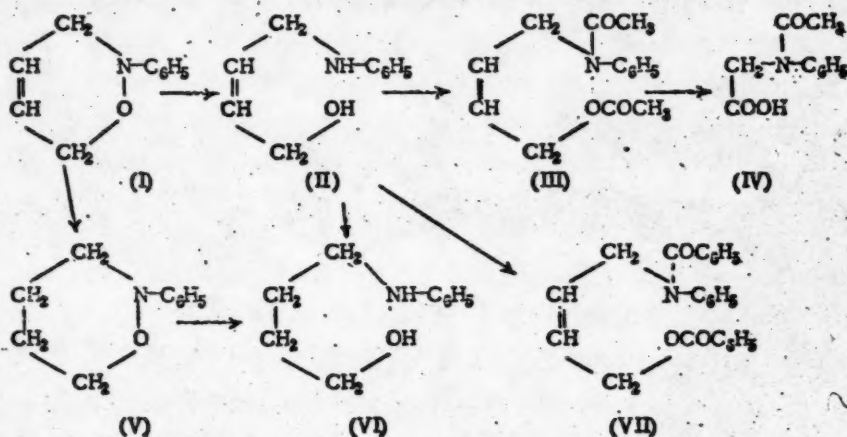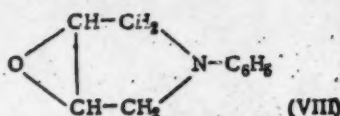

Catalytic hydrogenation of 2-phenyl-3,6-dihydro-ortho-oxazine (I) in presence of platinized charcoal gives 2-phenyltetrahydro-ortho-oxazine (V), which is reduced by zinc dust and acetic acid to 4-anilinobutan-1-ol (VI).

Catalytic reduction of 4-anilinobut-2-en-1-ol (II) should give 4-anilinobutan-1-ol (VI), but with platinized charcoal about 1.8 mol of hydrogen was absorbed per mol of 4-anilinobut-2-en-1-ol (II), giving a reaction product which boiled over a wide range of temperatures, and from which were isolated n-butanol, aniline, N-n-butylaniline, and 4-anilinobutan-1-ol (VI), obtained in only 17% yield, the basic products being butanol and aniline. These are produced probably by hydrogenolytic fission of 4-anilinobut-2-en-1-ol at the N-allyl bond, giving aniline and but-2-en-1-ol, which is further reduced to n-butanol. •

N-n-Butylaniline is probably formed by reduction of 4-anilinobut-2-en-1-ol to but-2-enylaniline, which is further reduced to N-n-butylaniline. After we had completed our study of the product of addition of butadiene to nitrosobenzene a paper on the same subject was published by Wichterle [6], who, however, came to the mistaken conclusion that it is 3,4-oxido-N-phenylpyrrolidine (VIII). After I had published my paper [7] Wichterle [8] admitted that he was wrong, and that the structure of the addition product given by me as structure (I) is the correct one.

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• The reaction of hydrogenolytic fission at the N-allyl bond has been described in the literature. Thus Klein-schmidt and Cope [1] found that hydrogenation in presence of palladized charcoal of crotylmethylaniline gives methylaniline. Cope, Estes, Emery, and Haven [2] found that dimethylamine is formed by hydrogenation in presence of palladized norite of trans-1,2-bis-(dimethylamino)-cyclopent-3-ene. Emde and Kull [3] showed that tralkylamine hydrochlorides are given by hydrogenation of allyltrialkylammonium or cinnamyltrialkylammonium chlorides in presence of platinum or palladium catalysts. Howton [4] showed that trimethylamine hydrobromide is obtained by hydrogenation of 2-cyclohexenyltrimethylammonium bromide in presence of platinum, nickel, or palladium. A number of authors [5] have studied the reaction of catalytic debenzylation of N-benzylamines.

$$\text{(VIII)}$$

CH—CH₂ structure with O, N—C₆H₅

The structure (VIII) shows a ring: O connected to two CH—CH₂ groups, and N—C₆H₅.

EXPERIMENTAL

Preparation of 2-phenyl-3,6-dihydro-ortho-oxazine

Experiment 1. 10.7 g (0.1 mole) of nitrosobenzene and 10.7 g of butadiene were placed in a tube which was cooled in a mixture of solid carbon dioxide and ethanol. The tube was sealed and left for 24 hours at 5-10° in a water bath. The tube was shaken from time to time during the first 5 hours, and the whole of the nitrosobenzene had passed into solution at the end of 6 hours. After 24 hours the originally green solution had become light brown, and light brown crystals had formed on the walls of the tube. The tube was cooled, opened, and unreacted butadiene was allowed to evaporate off. The residue was recrystallized from 30 ml of light petroleum, the hot solution being filtered, leaving about 0.6 g of an insoluble, yellow, finely crystalline substance, m.p. 181-184° (decomposition). Light yellow crystals were deposited by the cooled solution, and these were collected and washed with light petroleum. After two recrystallizations from 15 ml of ethanol a yield of 9.0 g (61% of theoretical) of a colorless, finely crystalline substance, m.p. 50-51°, was obtained.

Found %: C 74.70; 74.98; H 6.69; 6.63; N 8.72; 8.78
$C_{10}H_{11}ON$. Calculated %: C 74.50; H 6.88; N 8.69.

Experiment 2. A tube containing 10.7 g (0.1 mole) of nitrosobenzene and 21.4 g of butadiene was placed in an ice bath for a week, the tube shaken every 12 hours during the first 3 days. The tube was opened after 7 days, excess butadiene evaporated off, and the residue steam distilled. The crystalline product appearing in the distillate was collected and dried in a desiccator over H_2SO_4, giving 14.8 g (91% yield) of 2-phenyl-3,6-dihydro-ortho-oxazine, m.p. 49-50°. The light yellow product was recrystallized from ethanol; colorless product, m.p. 50-51°.

Found %: C 74.80; 74.84; H 6.83; 6.87; N 8.63; 8.61
$C_{10}H_{11}ON$. Calculated %: C 74.50; H 6.88; N 8.69

Experiment 3. 28 g of butadiene was introduced into a flask containing 26.8 g (0.25 mole) of nitrosobenzene, at 0°, and the flask was left on ice for some days, after which the solvent was distilled off, and the residue was vacuum distilled, giving 36.4 g (90% of theoretical) of 2-phenyl-3,6-dihydro-ortho-oxazine, b.p. 107-108° at 35 mm, affording colorless crystals, m.p. 50-51°, after recrystallization from ethanol.

Experiment 4. 28 g of butadiene was placed in a flask containing 26.8 g (0.25 mole) of nitrosobenzene in 500 ml of ether, at 0°. Two days later the ether was distilled off, and the residue was distilled in vacuum, giving 36.5 g (91% of theoretical) of 2-phenyl-3,6-dihydro-ortho-oxazine, b.p. 108-109° at 4 mm, m.p. after recrystallization from ethanol 50-51°.

Experiment 5. 110 g butadiene was added to 107.1 g (1 mole) nitrosobenzene in 1 liter chloroform, at 0°. The chloroform was distilled off after a few days at 0°, the residue distilled in vacuum, giving 154.0 g (95% of theoretical) of 2-phenyl-3,6-dihydro-ortho-oxazine, b.p. 108-109° at 4 mm, m.p. 50-51°, after recrystallization from methanol.

Found %: C 74.32; 74.23; H 6.84; 6.87; N 8.59; 8.42
$C_{10}H_{11}ON$. Calculated %: C 74.50; H 6.88; N 8.69

Reduction of 2-phenyl-3,6-dihydro-ortho-oxazine with zinc dust and acetic acid, to give 4-anilinobut-2-en-1-ol

20 g of zinc dust was added to 16.1 g (0.1 mole) of 2-phenyl-3,6-dihydro-ortho-oxazine in 200 ml of glacial acetic acid, in a 450 ml bottle, which was stoppered, and was shaken for 10 min., when a second 20 ml portion of zinc dust was added, followed by shaking for another 10 min.; there was a considerable temperature rise during the first shaking, and a much smaller one during the second. 200 ml of water, followed by 200 g sodium hydroxide, with cooling, were then added, and the mixture was steam distilled, collecting about 500 ml of distillate. The residue in the distilling flask was then filtered hot, and the cooled filtrate was extracted with 5 successive 100 ml portions of benzene. The benzene extract was washed with water*, the benzene was distilled off, and the residue was

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* The benzene extract should be well washed with water, as it was noticed that thermal decomposition of 4-anilinobut-2-en-1-ol takes place during its vacuum distillation if even traces of caustic alkali are present, giving aniline and tarry products. The following experiment was done, in view of this observation. A few lumps of fused potassium hydroxide were added to a solution of 12.5 g of 4-anilinobut-2-en-1-ol, b.p. 161-162°/4.5 mm, in 30 ml of dry benzene, the solution was filtered after 12 hours, the filtrate was distilled to remove benzene, and the residue was distilled from a metal bath, at 5 mm. Energetic decomposition began when the temperature reached 155°, and a low b.p. distillate, containing tar, was formed; fractionation of the distillate gave 4.3 g of aniline, b.p. 69° at 10 mm; d_4^{20} 1.0193; n_D^{20} 1.5360, identified as acetanilide, m.p. 113.5-114°.

fractionally distilled in vacuum, giving 13.3 g (82% of theory) of 4-anilinobut-2-en-1-ol, b.p. 151-152°/2 mm, d_4^{20} 1.0816; n_D^{20} 1.5867; found MR_D 50.69; calculated MR_D 49.44; EMR_D 1.25. The product is a colorless, viscous liquid, which becomes yellow on storage.

Found %:	C 73.56; 73.46;	H 8.19; 8.13;	N 8.83; 8.98
$C_{10}H_{13}ON$. Calculated %:	C 73.59;	H 8.03;	N 8.58
Found %:	[H'] 1.11; 1.11		
$C_{10}H_{11}ON[H']_2$ Calculated %:	[H'] 1.24		

Dibenzoyl derivative of 4-anilinobut-2-en-1-ol

Benzoyl chloride (14.1 g; 0.1 mol) was added in 5 portions during 30 min to 4.90 g (0.03 mol) of 4-anilinobut-2-en-1-ol and 60 ml of 10% caustic soda, shaking vigorously after each addition. Excess of benzoyl chloride was hydrolyzed by heating on the water bath, and the crystalline product was collected by filtration, washed with water, and dried in a desiccator over sulfuric acid. A yield of 10.5 g of dibenzoyl derivative of 4-anilinobut-2-en-1-ol, m.p. 87-90°, was obtained (94% of theory); the m.p. was 90-91° after 2 recrystallizations from ethanol.

Found %:	C 77.91; 78.01;	H 5.78; 5.72;	N 3.89; 3.90
$C_{24}H_{21}O_3N$. Calculated %:	C 77.61;	H 5.70;	N 3.77

Diacetyl derivative of 4-anilinobut-2-en-1-ol

A solution of 16.3 g (0.1 mol) of 4-anilinobut-2-en-1-ol in 60 ml of acetic anhydride was heated under reflux on a boiling water bath for 3 hrs, after which acetic acid and excess of acetic anhydride were distilled off under reduced pressure (50 mm), and the residue was distilled at 1 mm, giving 23.2 g (94% of theoretical) of the diacetyl derivative of 4-anilinobut-2-en-1-ol, with the following constants: b.p. 160-161°/ 1 mm; d_4^{20} 1.1053; n_D^{20} 1.5271; found MR_D 68.79; calculated MR_D 68.04*; EMR_D 0.75. The product was a colorless viscous liquid.

Found %:	C 67.80; 67.82;	H 6.93; 6.86;	N 6.04; 6.10
$C_{14}H_{17}O_3N$ Calculated %:	C 68.00;	H 6.93;	N 5.66

Oxidation of the diacetyl derivative of 4-anilinobut-2-en-1-ol to N-acetyl-N-phenylglycine

A solution of 4.7 g (0.03 mol) of potassium permanganate in 350 ml of dry acetone was added with constant stirring during 90 min to 2.47 g (0.01 mol) of the diacetyl derivative of 4-anilinobut-2-en-1-ol in 100 ml of dry acetone. The solution was filtered on the next day, and the deposit was washed with acetone, and extracted with 50 ml of water. The aqueous extract was extracted with chloroform, and was then made acid with hydrochloric acid. The precipitate was collected, washed with cold water, and dried in a desiccator over sulfuric acid; yield 1.20 g (62% of theory) of N-acetyl-N-phenylglycine, m.p. 191-193°, raised to 194-195° after recrystallization from hot water.

Found %:	C 62.26; 62.22;	H 5.73; 5.72;	N 7.17; 7.00
$C_{10}H_{11}O_3N$. Calculated %:	C 62.16;	H 5.74;	N 7.25

A mixture of our product with N-acetyl-N-phenylglycine, m.p. 193-195°, prepared by the method of Bischoff and Hausdoerfer [11], melted at 193.5-195°. Published m.p. data are 190-191° [10] and 194-195° [11].

Catalytic hydrogenation of 2-phenyl-3,6-dihydro-ortho-oxazine to 2-phenyl-tetrahydro-ortho-oxazine

Hydrogenation of 32.2 g (0.2 mol) of 2-phenyl-3,6-dihydro-ortho-oxazine in 200 ml of cyclohexane was effected at room temperature and atmospheric pressure, in presence of 3 g of platinized charcoal (10% Pt), being completed in 2 hrs, when 4690 ml of hydrogen (at N.T.P.) had been adsorbed. The catalyst was filtered off, and the cyclohexane distilled off, the residue being fractionally distilled in vacuum, giving 25.4 g (78% of theory) of 2-phenyltetrahydro-ortho-oxazine, with the following constants: b.p. 104-105°/4 mm, d_4^{20} 1.0593; n_D^{20} 1.5550; found MR_D 49.45; calculated MR_D 47.80**; EMR_D 1.65. The product was a colorless, fairly mobile liquid,

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* The value of 2.49 was taken for amide nitrogen, in calculating molecular refraction [9].

** In calculating molecular refraction a value of 2.48 was taken for hydroxylamine nitrogen [12]. Kleinschmidt and Cope [1] showed that β-arylhydroxylamines display exaltation, varying from 1.09 to 1.5.

rapidly yellowing on storage.

Reduction of 2-phenyltetrahydro-ortho-oxazine by zinc dust and acetic acid, to 4-anilinobutan-1-ol

40 g of zinc dust was added in four portions during 20 min to a solution of 16.3 g (0.1 mol) of 2-phenyl-tetrahydro-ortho-oxazine in 200 ml of glacial acetic acid, in a bottle, which is stoppered and shaken after each addition. A considerable temperature rise was observed after adding the first and second portions of zinc dust, but not with subsequent portions. 200 ml of water, followed by 200 g of sodium hydroxide, with cooling, were added to the reaction mixture, which was then steam-distilled, to remove volatile products, collecting about 500 ml of distillate. The residue in the distilling flask was filtered hot, and the cooled filtrate was extracted with 5 successive portions of benzene. The benzene extract was washed with water, the benzene was distilled off, and the residue was fractionally distilled in vacuum, giving 7.7 g (47% of theory) of 4-anilinobutan-1-ol, with the following constants: b.p. 154-155°/3 mm, d_4^{20} 1.0498; n_D^{20} 1.5636; found MR_D 51.15; calculated MR_D 49.91; EMR 1.24. The product is a viscous colorless liquid, turning yellow on keeping. Published physical data are: b.p. 157°/3 mm; d_4^{20} 1.0508; n_D^{20} 1.5629 [8].

4-Anilinobut-1-yl hydrogen oxalate

A solution of 0.38 g (0.003 mol) of oxalic acid dihydrate in 2.1 ml of ethanol is added to 0.5 g (0.003 mol) of 4-anilinobutan-1-ol, and the salt separating is collected and washed with ethanol; yield, 0.61 g of acid oxalate, colorless needles, m.p. 124.5-125° (decomposition) (published m.p. 124.8-125° (decomposition) [8]).

Catalytic hydrogenation of 4-anilinobut-2-en-1-ol

Four experiments on the catalytic hydrogenation of 4-anilinobut-2-en-1-ol at room temperature and ordinary pressure were performed, with platinized charcoal catalyst. For each experiment 8.16 g (0.05 mol) of 4-anilino-but-2-en-1-ol in 70 ml of ether, and 2 g of platinized charcoal (5% Pt) were taken; the results obtained are given in the Table.

TABLE

Expt. No.	Duration of experiment	Ml of hydrogen absorbed, (0°/760 mm)
1	3 hrs. 45 min	1990
2	3 " 30 "	1985
3	3 " 15 "	1955
4	3 " 30 "	1985

The catalyzates from all 4 experiments were united, the ether was distilled off, and the residue was fractionally distilled, giving the following products: (a) n-butanol, (b) aniline, (c) N-n-butylaniline, and (d) 4-anilinobutan-1-ol.

(a) n-Butanol (4.72 g) had the following constants: b.p. 116.5-117.5°/742 mm; d_4^{20} 0.8099; n_D^{20} 1.4008. Published values are: b.p. 117.7°/760 mm; d_4^{20} 0.810; n_D^{20} 1.3993 [13].

n-Butanol was further identified by preparing the α-naphthyl-urethane. A mixture of 1.6 g of the fraction, b.p. 116.5-117.5°/742 mm, and 3.4 g of α-naphthyl isocyanate was heated until reaction commenced, and was then left until the next day. The n-butyl-α-naphthylurethane was twice recrystallized from n-heptane, when it melted at 70.5-71.5°.

The mixed m.p. with n-butyl-α-naphthylurethane prepared from a known sample of pure n-butanol was 70.5-71.5°; published m.p. are 71-72° [14] and 70° [15].

(b) Aniline (8.71 g) had the following constants: b.p. 184-185°/750 mm; d_4^{20} 1.0175; n_D^{20} 1.5847.; published values, b.p. 184.4°/760 mm; d_4^{20} 1.022; n_D^{20} 1.5863 [13]. Acetanilide, m.p. 113-114°, was prepared for further identification.

(c) N-n-Butylaniline (2.53 g) had the following physical constants: b.p. 95-96°/4.5 mm; d_4^{20} 0.9394; n_D^{20} 1.5393; found MR_D 49.78; calculated MR_D 48.38; EMR_D 1.40. Published values are: b.p. 115-120°/15 mm; d_4^{20} 0.9358; n_D^{20} 1.5381; b.p. 112-114°/9 mm; d_4^{20} 0.9362; n_D^{20} 1.5373 [16].

N-n-Butylbenzanilide was prepared from 2.0 g of the fraction of b.p. 95-96°/4.5 mm and 2.8 g of benzoyl chloride, with 15 ml of 10% caustic soda solution. The crystalline product was dissolved in ether, and the solution was washed successively with water, 5% hydrochloric acid, 5% caustic soda, and water, and dried with anhydrous sodium sulfate. The ether was then distilled off, giving 3.2 g of N-n-butylbenzanilide, which melted at 49-51° after two recrystallizations from n-heptane.

Found %: N 5.58; 5.71
$C_{17}H_{19}ON$. Calculated %: N 5.53

The mixed m.p. with known N-n-butylbenzanilide, m.p. 53-54°, was 49-51.5°. Published m.p. are 55° [17] and 47-48° [18].

(d) 4-Anilinobutan-1-ol (5.70 g) had the following constants: b.p. 147-148°/1.5 mm; d_4^{20} 1.0491; n_D^{20} 1.5638; found MR_D 51.20; calculated MR_D 49.91; EMR_D 1.29.

Found %: N 8.46; 8.66
$C_{10}H_{15}ON$. Calculated %: N 8.48

It was identified as the acid oxalate. A solution of 1.26 g of oxalic acid dihydrate in 7 ml of ethanol was added to 1.65 g of the fraction of b.p. 147-148°/1.5 mm, to give 2.18 g of acid oxalate, which was collected and washed with ethanol. It melted at 124.5-125° (decomposition) after recrystallization from methanol.

Found %: N 5.51; 5.65
$C_{12}H_{17}O_5N$. Calculated %: N 5.49

The m.p. was not changed by mixing with 4-anilinobut-1-yl hydrogen oxalate obtained by reduction of 2-phenyl-3,6-dihydro-ortho-oxazine with zinc dust and acetic acid.

I would like, in conclusion, to express my deep indebtedness to A. N. Nesmeyanov for advising me to study the reaction of diene hydrocarbons with nitrosobenzene, for his unfailing interest in my work, and his valuable advice on its execution.

SUMMARY

1. The reaction between nitrosobenzene and buta-1,3-diene has been studied.

2. Addition takes place according to the diene synthesis, with formation of 2-phenyl-3,6-dihydro-ortho-oxazine.

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STUDIES OF QUINOLINE DERIVATIVES

## PART I. N-ARYL QUATERNARY SALTS OF QUINOLINE DERIVATIVES

G. T. Pilyugin

Quaternary salts of heterocyclic based with an alkyl or alkyl-aromatic radical attached to the cyclic nitrogen atom are usually prepared by heating the appropriate bases with alkyl halides, sulfates, or aryl-sulfonates. N-Aryl salts cannot, however, be prepared by this general method, since aryl halides or aryl-sulfonates do not give quaternary salts when heated with heterocyclic bases, in view of their low mutual reactivity. This was one of the reasons for the absence from the literature of such quaternary salts and of their derivatives with aryl radicals attached to the cyclic N atom. Herein, too, lies the difficulty of synthesizing N-aryl cyanine dyes of different classes, for which quaternary salts are the basic products.

Kiprianov, Ushenko, and Asnina obtained N-aryl quaternary salts from thiazole derivatives, and used them for the cyanine condensation [1]. Literature references to N-aryl quaternary salts prepared from pyrrole and indolenine derivatives, which are converted into pyrrolo- and indo-cyanines, are to be found [2]. Yet, although heterocyclic compounds containing the quinoline nucleus are among the most commonly encountered of heterocyclic compounds, the N-aryl quaternary salts of quinoline derivatives and their diverse transformations have not been studied at all by organic chemists. For this reason the preparation and study of such salts are of considerable theoretical and practical importance.

We have elaborated a general method for the preparation of N-aryl and N-alkyl quaternary salts of quinoline derivatives. In view of the inapplicability of the usual method, the method depended on the presence of the appropriate aryl or alkyl radical attached to the N atom of the original substance used for synthesis of the heterocycle. These starting substances were secondary arylamines, in which the imino hydrogen is relatively very mobile.

Secondary arylamines and alkarylamines were condensed with paraldehyde or acetaldehyde in acid solution to give N-arylquinoline derivatives (see formulas below).

Thus, for example, the aryl halide salts of quinaldine and its derivatives were obtained from diphenyl-amine or its derivatives. A study of this reaction showed that it was very convenient to combine cyclization with conversion of the base so obtained into its quaternary salt, both for their subsequent application to the cyanine condensation and for preparation of quinolines and methyleno-derivatives.
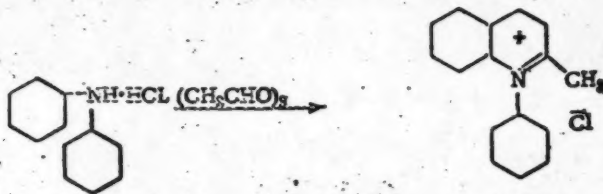
The quaternary salts were prepared by heating the secondary arylamines with paraldehyde and hydro-chloric or chloric acid in benzene or dioxan solution, in sealed glass tubes at 100°. The quaternary salts obtained were prepared and examined by standard methods. They had definite m.p., and they readily underwent the cyanine condensation, leaving no doubt as to their purity and structure. The arylquinolinium salts obtained are shown in the Table.

Condensation, to give N-aryl quaternary salts, was found to occur in presence of chloric acid, which not only serves as a condensing agent, but also forms the relatively insoluble perchlorate. It was found that attachment
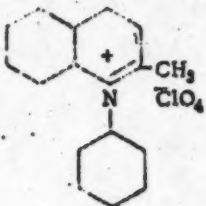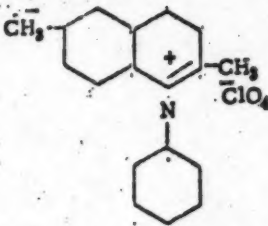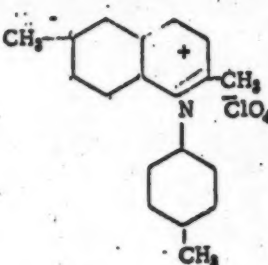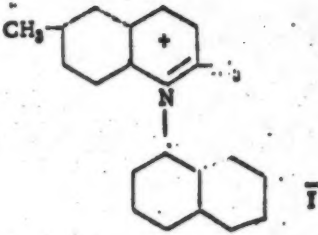
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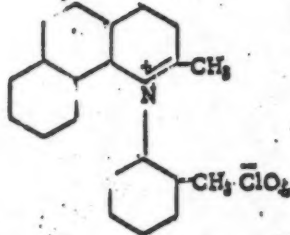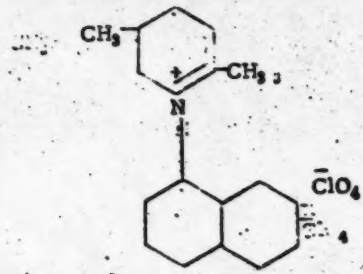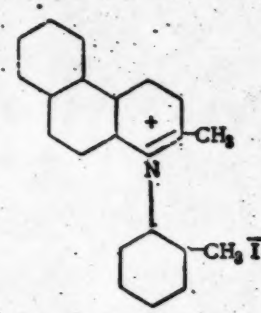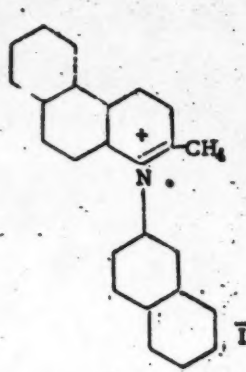
Initial amine	Formula of the quaternary salt obtained	M.p. °C	Yield, %
Diphenylamine		159-160	10.0
4-Methyldiphenylamine		154-155	25.0
4,4'-Dimethyldiphenylamine		193-194	16.0
p-Tolyl-α-naphthylamine		199-200	22.0
o-Tolyl-α-naphthylamine		174-175	15.0

| Initial amine	Formula of the quaternary salt obtained	M.p. °C	Yield, %
Phenyl-α-naphthylamine		220	25.0
o-Tolyl-β-naphthylamine		173-174	18.6
β,β'-Dinaphthylamine		200-203	23.0

of an aryl radical to the heterocyclic nitrogen activates an α-methyl group, as was shown by the ease with which cyanine condensation of trinuclear quaternary cyanine salts of halogen acids, but not of sulfonic acids, took place, on the one hand, and by the fact that the quinocyanine condensation proceeds with orthoacetic ester, which is not the case with N-alkyl quaternary salts.

The reactivity of α-methyl groups is thus much greater when an aryl radical is attached to the cyclic nitrogen atom than with an alkyl radical; this difference is due to modified electronic equilibria in that part of the molecule, which also lead to other changes in the properties of the quaternary salts and of the derived dyes. Thus, N-phenyl quaternary salts have lower m.p. and higher solubilities than do the corresponding N-alkyl salts.

The secondary arylamines condensed by us with paraldehyde may yield only a single product, when they have symmetrical molecules (a), or there is an equal probability of forming two products, when the amine is dissymmetrical (b):

(a)

(b)
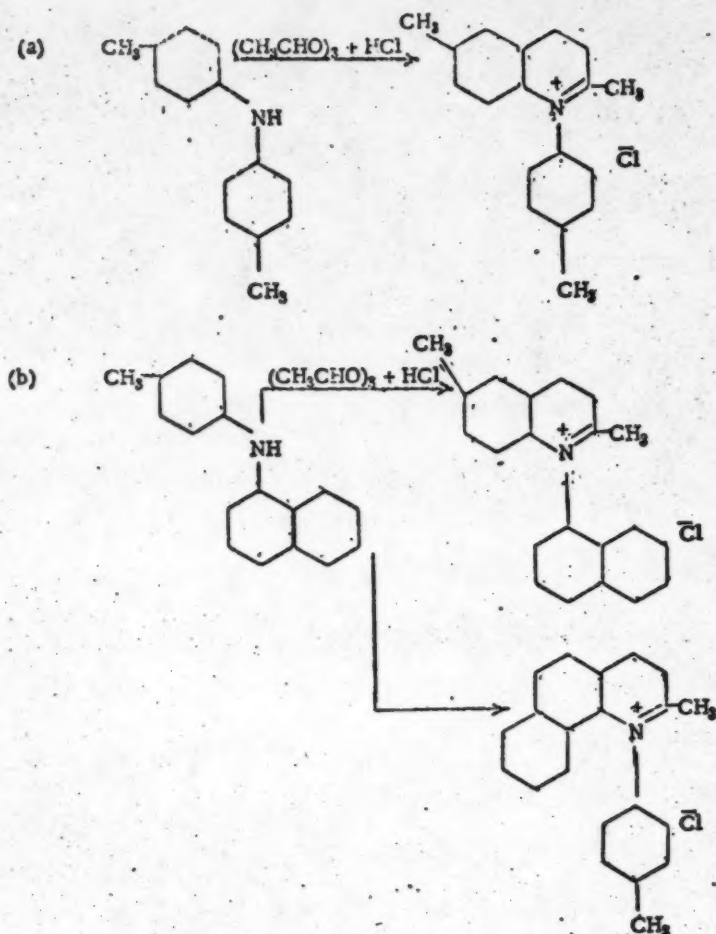
The formation of a third product is possible, although highly improbable, when the dissymmetrical amine contains a β-naphthyl radical
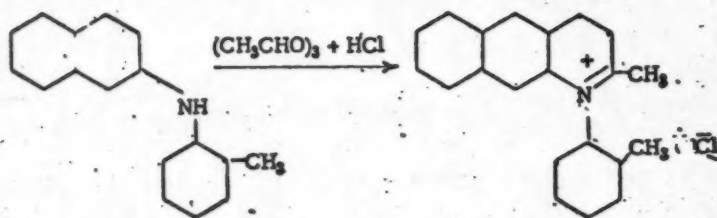
The low probability of this cyclization follows from the preponderance of single bonds between the β,β-atoms of the naphthalene ring, and of double bonds between the α- and β-atoms, as is indicated by numerous known experimental examples. Thus coupling of β-naphthol with diazonium salts takes place exclusively in the α-position, and in the condensation of β-naphthylamine with glycerol the quinoline ring is always closed at the α-atom, and never at the β-carbon atom. In case (b) the quantitative course of the cyclization reaction depends not only on the reactivity of the given radicals, but also on the conditions of cyclization.

Under the fairly uniform conditions in which we conducted the reaction only in two cases did we observe formation of isomeric quaternary salts from dissymmetric amines, to any appreciable extent. Thus 4-methyl-diphenylamine may undergo cyclization in the following ways:
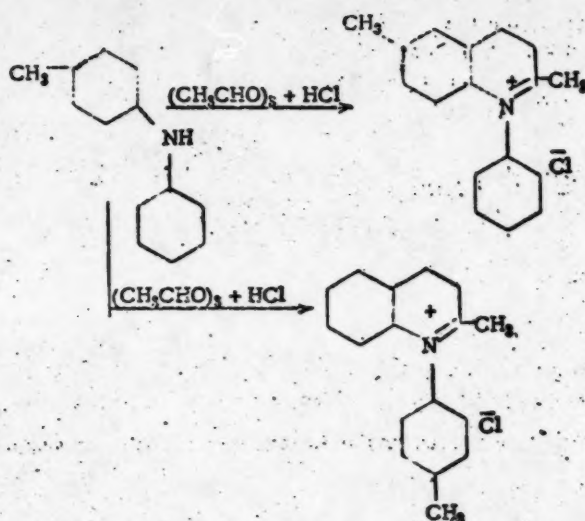
From the theoretical point of view, the probability of formation of quaternary salt of N-phenyl-6-methylquinaldine is the greater one, since the electron donor methyl group substituted in the benzene ring should activate it. We did not, in fact, observe, under our experimental conditions, the less probable case of cyclization with production of N-p-tolylquinaldine. This is confirmed by the fact that the product is a single substance, and by the absorption maximum at 620 mμ of the dye prepared from it. Otherwise the absorption maximum of the dye would tend towards a limiting value of 614 mμ (absorption maximum of a dye with a N-phenyl group); in all probability it would deviate from this value towards the ultraviolet end of the spectrum, as a result of the greater basicity of the p-tolyl than of the phenyl group.

Condensation of p-tolyl-α-naphthylamine may involve two forms of cyclization:
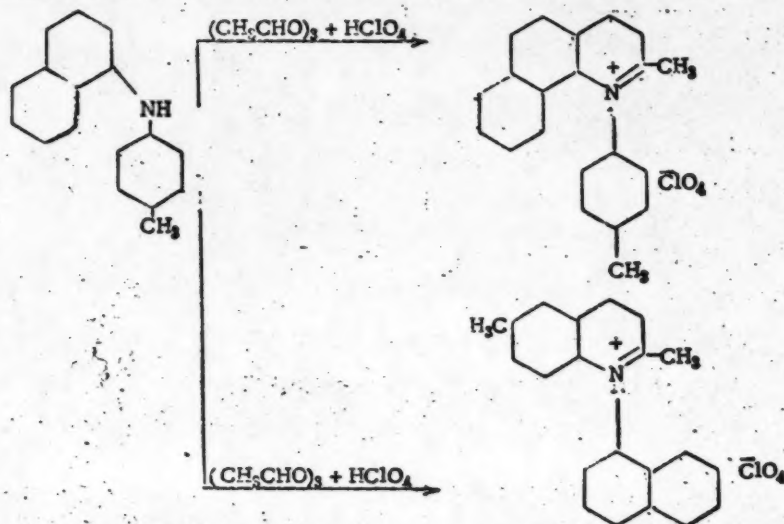
Here, for the same reasons, we may expect that cyclization will take place according to the second variant, with formation of quaternary salt of N-(α-naphthyl)-6-methylquinaldine. The product is a single substance, yielding a carbocyanine with an absorption maximum at 625 mμ, whereas with cyclization in the other direction the absorption maximum of the derived dye would exceed that of the known carbocyanine
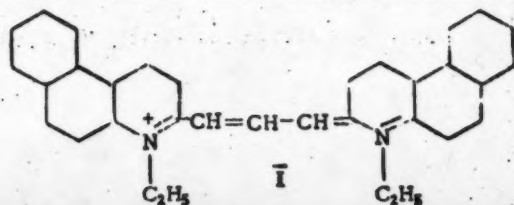
of 634 mμ [3]. There can be no doubt that a similar dye not containing a N-p-tolyl group would have an absorption maximum shifted still further towards the red end of the spectrum, which is not in fact the case. We similarly established that condensation takes place in one direction only with phenyl-α-naphthylamine
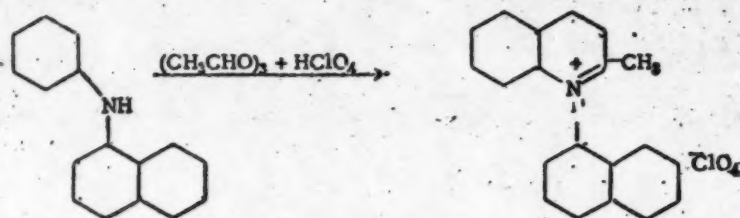
as is shown by the preparation from it of a quinocarbocyanine with an absorption maximum at 618 mμ.

Two isomeric products were given by o-tolyl-α-naphthylamine and by o-tolyl-β-naphthylamine:

(a)

(b)
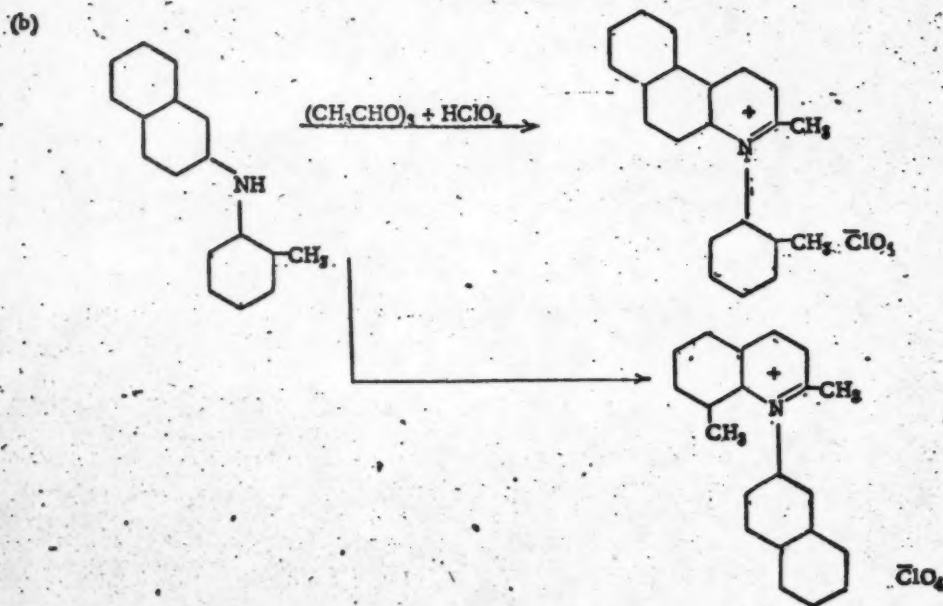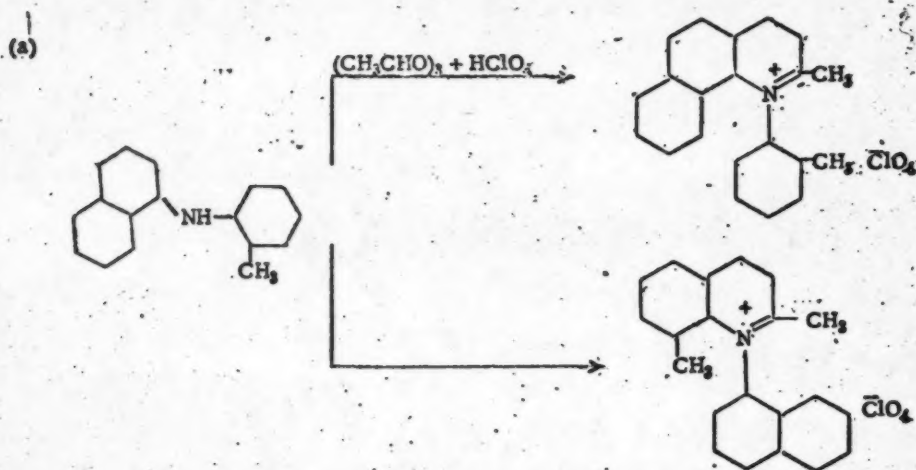
The main reaction products were quaternary salts with N-o-tolyl groups. The green carbocyanines prepared therefrom had the following optical properties:

(a) bis-[N-o-tolyl-7,8-benzoquinoline-(2)]-trimethinecyanine perchlorate — absorption maximum in ethanol 642 mμ.

(b) bis-[N-o-tolyl-5,6-benzoquinoline-(2)]-trimethinecyanine perchlorate — absorption maximum 644 mμ.

The isomeric quaternary salts with N-α- or N-β-naphthyl radicals were obtained in small yields only. They gave positive reactions for formation of blue quinocarbocyanines, which are being studied by us. Thus the quaternary salts with N-aryl groups, derivatives of quinaldine, have so far been introduced into the cyanine condensation only, for the purpose of preparing sensitizing dyes.

EXPERIMENTAL

N-Phenylquinaldine perchlorate. 4 g of diphenylamine hydrochloride was heated at 80-110° with 2 g of paraldehyde in dioxan, in a sealed tube. The semi-solid, tacky product was washed with ether, and was taken without further purification for cyanine condensation with orthoformic acid, which proceeded smoothly. This condensation product was extracted repeatedly with boiling ethanol, and the extract was evaporated to dryness, leaving a dark-colored, sticky residue, which was washed 2-3 times with ether, and dissolved in a small volume of ethanol. The quaternary salt was precipitated from this solution by adding a saturated solution of potassium perchlorate. The light brown precipitate was filtered off, and the filtrate was evaporated on the water bath until drops of oil formed, when it was cooled and filtered; the quaternary salt collected was recrystallized from water. N-Phenyl-quinaldine crystallizes in needles, m.p. 159-160°, of a faint yellow color. It is readily soluble in ethanol and in hot water, and is sparingly soluble in cold water. The yield is 10% of theoretical.

Found %: Cl 11.32
$C_{16}H_{14}NClO_4$. Calculated %: Cl 11.50

N-Phenyl-6-methylquinaldine perchlorate. 3.3 g of 4-methyldiphenylamine, 2.5 ml of benzene, 1.5 ml of 35% chloric acid, and 1.8 ml of paraldehyde were heated in a sealed tube for 10 hrs at 100°, giving a thick, dark red liquid. The product was washed with a few portions of ether, and was dissolved in a small volume of ethanol, from which it crystallized out. Recrystallization from ethanol gave 1.35 g (25% of theoretical) of light orange, finely crystalline product, m.p. 154-155°.

Found %: Cl 10.40
$C_{17}H_{16}NClO_4$. Calculated %: Cl 10.66

N-(p-tolyl)-6-methylquinaldine perchlorate. 2 g of 4,4'-dimethyl-diphenylamine, 2 ml of benzene, 2 ml of 35% chloric acid, and 1.4 ml of paraldehyde (added at 0°) were heated at 100° for 15 hrs in a sealed tube; the use of more concentrated chloric acid led to formation of tarry products. Shortening the reaction time lowers the yield of quaternary salt, whereas prolonging it leads to deterioration in the quality of the salt, and renders its purification difficult. The reaction product, which was a viscous, dark red liquid, was washed with small portions of ether, until the ether ceased to be colored, and the residue was dissolved in a small volume of ethanol, from which the salt crystallized. The salt was washed with alcohol and ether, and recrystallized from ethanol, giving 0.55 g (16% of theoretical) of colorless finely crystalline salt, m.p. 193-194°.

Found %: Cl 10.22
$C_{18}H_{18}NClO_4$. Calculated %: Cl 10.33

N-(α-naphthyl)-6-methylquinaldine iodide. 2 g p-tolyl-(α-naphthyl)-amine, 2 ml of benzene, 1 ml of hydrochloric acid, and 1.5 ml of paraldehyde were heated in a sealed tube for 10 hrs at 100° giving a dark red viscous oil, which solidified after extraction with ether. The product was repeatedly extracted with boiling ethanol, until the extract became colorless. The hot extract was filtered and evaporated down to small volume, when 4 ml of saturated potassium iodide solution was added, the solution was boiled, and filtered hot. The filtrate was evaporated until an oily surface film appeared, when it was left overnight and filtered in the morning. The yellow crystalline product (yield 22% of theory) melts at 199-200° (decomposition).

Found %: I 30.48
$C_{21}H_{18}NI$. Calculated %: I 30.83

N-(o-tolyl)-7,8-benzoquinaldine perchlorate. A mixture of 3.8 g of o-tolyl-α-naphthyl-amine, 2.2 g of paraldehyde, 1.5 ml of hydrochloric acid (d 1.19) and 4 ml of benzene in a sealed tube was cooled strongly, shaken vigorously, and heated in a boiling water bath for 8 hrs. The product was a gelatinous, bordeaux-colored mass, which was extracted with ether until the extracts became colorless; the residue was then a yellow powder. This powder was extracted repeatedly with boiling ethanol, the extract was evaporated down to small volume, and saturated aqueous potassium perchlorate was added, to give a salt which melted at 173-174°, after recrystallization from aqueous ethanol; yield 15% of theoretical.

Found %: Cl 9.16
$C_{21}H_{18}NClO_4$. Calculated %: Cl 9.37

N-α-naphthylquinaldine perchlorate. 2 g of N-α-naphthylaniline, 1.3 ml of paraldehyde, 0.5 ml of 38% chloric acid, and 2 ml of benzene were heated at 100° for 10 hrs, in a sealed tube. The dark red product was extracted with ether, when it became solid, and was recrystallized from ethanol, giving a finely crystalline powder, which was collected, washed with ether, and recrystallized from aqueous ethanol, giving 1.8 g (25% of theoretical) of salt, m.p. 220° (decomposition).

Found %: Cl 9.44
$C_{20}H_{16}NClO_4$. Calculated %: Cl 9.60

N-(o-tolyl)-5,6-benzoquinaldine iodide. A mixture of 3.4 g of o-tolyl-β-naphthylamine, 1.9 g of paraldehyde, 1.4 g of hydrochloric acid (d 1.19), and 2 ml of benzene was heated at 100° for 16 hrs, in a sealed tube. The solid product was repeatedly extracted with ether, and then dissolved in 10 ml of boiling ethanol. Saturated aqueous potassium iodide was added to the solution, from which the quaternary salt separated on cooling. It was collected, washed with ether, dried, and recrystallized from aqueous ethanol, giving 1.1 g (18.6% of theoretical) of a yellowish, finely crystalline product, m.p. 173°.

Found %: I 31.40
$C_{21}H_{16}NI$. Calculated %: I 31.95

N-β-naphthyl-5,6-benzoquinaldine iodide. A mixture of 3 g of β,β'-dinaphthylamine, 1.6 g of paraldehyde, 1 ml of hydrochloric acid (d 1.19), and 3 ml of benzene was heated at 100° for 8 hrs, in a sealed tube. The dark red, viscous, oily product was repeatedly extracted with ether, until the extracts became colorless. The bordeaux-colored, semi-solid residue, which consists chiefly of quaternary salt is extracted 2-3 times with small portions of hot ethanol, and 4 ml of saturated aqueous potassium iodide was added to the dark red extract, giving a light brown precipitate of quaternary salt, which is collected, washed with ether, and dried at 110°; yield of crude salt 70% of theory. The salt gave the cyanine condensation reaction. Recrystallization from aqueous ethanol gave 1.6 g (32% of theory) of pale yellow crystalline salt, m.p. 200-203°.

Found %: I 28.10
$C_{24}H_{18}NI$. Calculated %: I 28.35

SUMMARY

1. Condensation of secondary arylamines with paraldehyde gives a series of N-aryl substituted quinolines.

2. Eight quaternary N-arylquinolinium salts have been prepared and described, in which the N-aryl radical is phenyl, o-tolyl, p-tolyl, α-naphthyl, and β-naphthyl.

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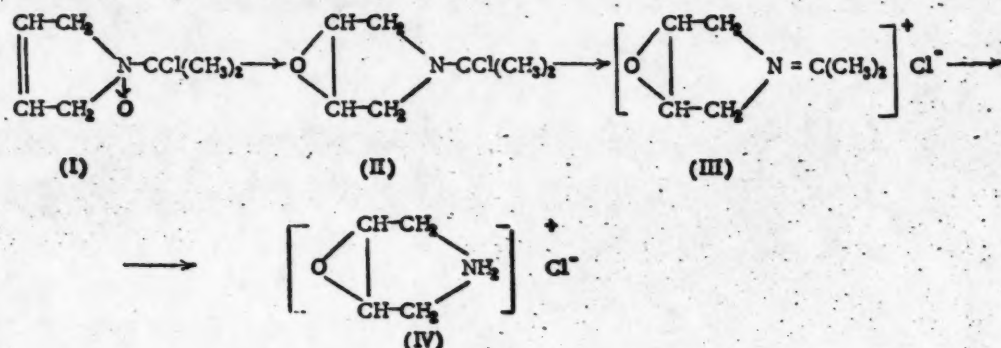
REACTIONS OF DIENE HYDROCARBONS WITH NITROSO-COMPOUNDS

REACTION OF BUTA-1,3-DIENE, 2,3-DIMETHYLBUTA-1,3-DIENE, AND CYCLOHEXA-1,3-DIENE WITH 1-CHLORO-1-NITROSOCYCLOHEXANE

Yu. A. Arbuzov and A. Markovskaya

Wichterle [1] found in 1947 that buta-1,3-diene reacts with 2-chloro-2-nitrosopropane in benzene, in presence of ethanol, to give a crystalline product, C_6H_8ONCl, m.p. 153°. The product obtained in absence of ethanol is a tarry substance, insoluble in benzene, which was converted into the above substance, m.p. 153°, by treatment with a small amount of water or ethanol. The same product is obtained from buta-1,3-diene and 1-chloro-1-nitrosocyclohexane in benzene and ethanol as with 2-chloro-2-nitrosopropane. By the action of alkali on an aqueous solution of the substance of m.p. 153° Wichterle obtained a liquid product, b.p. 50-52°/20 mm, which he supposed to be 3,4-oxidopyrrolidine, of which the substance of m.p. 153° was the hydrochloride.

Wichterle explained the formation of this hydrochloride in the following way. The first product of the reaction between butadiene and 2-chloro-2-nitrosopropane is the N-oxide (I), which undergoes transformation into a 3,4-oxidopyrrolidine derivative (II), which is a chloride of the pseudo-base. Compound (II) undergoes further rearrangement to the quaternary salt (III), which then undergoes hydrolysis or alcoholysis to give 3,4-oxidopyrrolidine hydrochloride (IV):

It has been shown [2-5] that diene hydrocarbons react with aromatic nitroso-compounds according to the diene synthesis, with formation of 3,6-dihydro-ortho-oxazine derivatives.

It was reasonable to suppose that the reaction of buta-1,3-diene with chloronitroso-compounds should also proceed according to the diene synthesis with formation of the N-derivative of 3,6-dihydro-ortho-oxazine (V), which then undergoes hydrolysis (or alcoholysis), with formation of 3,6-dihydro-ortho-oxazine hydrochloride (VI). Wichterle's base, b.p. 50-52°/20 mm, should thus have the structure of 3,6-dihydro-ortho-oxazine (VII).
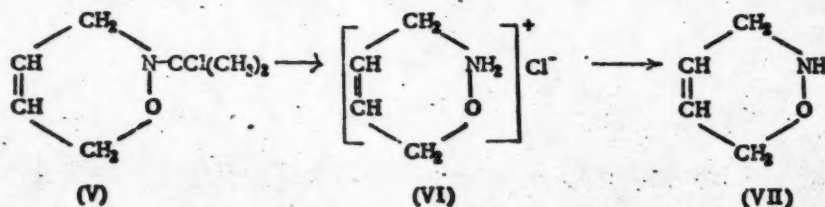
Confirmation of the correctness of structure (VII) for the base C_4H_7ON was provided in 1949 by Finkelshtein, Arbuzov, and Shorygin [6], who showed that the Raman spectrum of this base (b.p. 50.5°/19 mm; d_4^{20}

355

1.0714; n_D^{20} 1.4893) contained a frequency corresponding to a C=C bond, with an intensity characteristic of an isolated C=C bond. In 1950 Wichterle and Novak [7] published a paper in which they admitted the correctness of Yu. A. Arbuzov's 3,6-dihydro-ortho-oxazine structure (VII) for the base C_6H_7ON.

The present paper describes the results of a study of the reactions between buta-1,3-diene, 2,3-dimethyl-buta-1,3-diene, and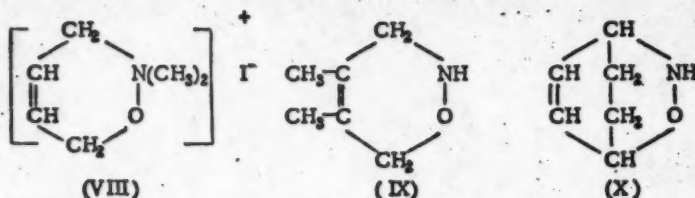 cyclohexa-1,3-diene with 1-chloro-1-nitrosocyclohexane in ethereal solution, in presence of ethanol. Buta-1,3-diene and 1-chloro-1-nitrosocyclohexane gave 3,6-dihydro-ortho-oxazine hydrochloride (VI), from which 3,6-dihydro-ortho-oxazine (VII) was obtained; a number of its derivatives was prepared for its identification, such as the methiodide of 2-methyl-3,6-dihydro-ortho-oxazine (VIII), from methyl iodide and 3,6-dihydro-ortho-oxazine (VII), and the 3,5-dinitrobenzoyl and 2,4-dinitrophenyl derivatives and the picrate, by standard methods.

1-Chloro-1-nitrosocyclohexane and 2,3-dimethylbuta-1,3-diene give 4,5-dimethyl-3,6-dihydro-ortho-oxazine hydrochloride, from which the free base (IX) is prepared; its picrate and 3,5-dinitrobenzoate are described.

(VIII)   (IX)   (X)

1-Chloro-1-nitrosocyclohexane and cyclohexa-1,3-diene afford 3,6-endoethyleno-3,6-dihydro-ortho-oxazine hydrochloride, from which the free base (X), a colorless, waxy substance, was obtained, as well as its crystalline picrate and benzoyl and 3,5-dinitrobenzoyl derivatives.

EXPERIMENTAL

3,6-Dihydro-ortho-oxazine hydrochloride. 62 g of buta-1,3-diene was added to a solution of 59.0 g (0.4 mol) of 1-chloro-1-nitrosocyclohexane in 150 ml of ether and 58 ml of ethanol, at 0°. Colorless needle-shaped crystals began to separate within 30 minutes. The flask was left for 3 days at 0°, during which time the color of the solution changed from blue-violet to light brown. The crystalline deposit was collected and washed with absolute ether, giving 35.2 g (72.4% of theoretical) of hydrochloride, m.p. 149-151° (decomposition), rising to 151-152° (decomposition) after recrystallization from absolute ethanol.

Found %: Cl 29.11; 29.24
C_4H_8ONCl. Calculated %: Cl 29.17

3,6-Dihydro-ortho-oxazine. 45 g of caustic potash was added gradually, cooling at 0°, to a solution of 48.6 g (0.4 mol) of 3,6-dihydro-ortho-oxazine hydrochloride in 40 ml of water, the potassium chloride forming was filtered off, and the filtrate was thrice extracted with ether. The combined ethereal extracts were dried with fused potassium hydroxide, and the ether was distilled off, giving 30.9 g (90.9%) of 3,6-dihydro-ortho-oxazine, a colorless mobile liquid having the following constants: b.p. 50.5-51°/19 mm; d_4^{20} 1.0702; n_D^{20} 1.4891; found MR_D 22.95; calculated MR_D 23.23.

Found %: C 56.37; 56.28; H 8.27; 8.29; N 16.30; 16.31
C_4H_7ON. Calculated %: C 56.45; H 8.29; N 16.46

The picrate of 3,6-dihydro-ortho-oxazine crystallizes from water as long yellow needles, m.p. 163-164° (decomposition).

Found %: N 17.77; 17.57
$C_{10}H_{10}O_8N_4$. Calculated %: N 17.83

2-Methyl-3,6-dihydro-ortho-oxazine methiodide. 5 ml of methanol, 1.7 g of sodium bicarbonate, and 5 ml of methyl iodide were added to 1.22 g (0.01 mol) of 3,6-dihydro-ortho-oxazine hydrochloride, and the mixture was boiled under reflux for $2\frac{1}{4}$ hrs., and was filtered hot. Platelets of 2-methyl-3,6-dihydro-ortho-oxazine methiodide, m.p. 132.5-133° (decomposition) after recrystallization from methanol, separated from the filtrate on cooling, in 83% yield (2.0 g). The m.p. given by Wichterle and Novak [7] is 133° (decomposition).

Found %: I 52.87; 52.91
$C_6H_{12}ONI$. Calculated %: I 52.65

<u>2-(3',5'-dinitrobenzoyl)-3,6-dihydro-ortho-oxazine.</u> A mixture of 0.61 g (0.005 mol) of 3,6-dihydro-ortho-oxazine hydrochloride, 1.15 g (0.005 mol) of 3,5-dinitrobenzoyl chloride, and 2 ml of dry pyridine was heated at 100° for 10 min, cooled, and treated with 3 N hydrochloric acid. The precipitate was collected, washed with 5% hydrochloric acid, 2% aqueous sodium carbonate, and water, successively, and recrystallized from methanol, giving 0.61 g (43.6%) of faint yellow crystals, m.p. 142.5°.

Found %: C 47.38; 47.42; H 3.40; 3.34; N 14.92; 14.96
$C_{11}H_9O_6N_3$. Calculated %: C 47.32;   H 3.25;   N 15.05

<u>2-(2',4'-dinitrophenyl)-3,6-dihydro-ortho-oxazine.</u> A mixture of 0.43 g (0.005 mol) of 3,6-dihydro-ortho-oxazine, 1.01 g (0.005 mol) of chloro-2,4-dinitrobenzene, 0.6 g of anhydrous potassium acetate, and 10 ml of absolute alcohol were heated at 100° under reflux for 2 hrs and 20 ml of water was added to the cooled mixture. The precipitate was collected, washed with water, and recrystallized from acetone, giving 0.66 g (52.4%) of large yellow crystals, m.p. 142.5° (decomposition).

Found %: N 16.42; 16.39
$C_{10}H_9O_5N_3$. Calculated %: N 16.73

<u>4,5-Dimethyl-3,6-dihydro-ortho-oxazine hydrochloride.</u> 22.2 g (0.27 mol) of 2,3-dimethylbuta-1,3-diene was added to a solution of 36.9 g (0.25 mol) of 1-chloro-1-nitrosocyclohexane in 90 ml of ether and 33 ml of ethanol at 0°, and the mixture was kept at 0° for 12 hrs and at room temperature for 3 days, during which time its color changed from blue-violet to green. The crystalline deposit was collected and washed with ether; yield 13.0 (34.8%), m.p. 149-150° (decomposition), after recrystallization from absolute alcohol.

Found %: C 48.00; 47.90; H 8.16; 8.29; N 9.27; 9.22; Cl 24.21; 24.32
$C_6H_{12}ONCl$. Calculated %: C 48.16;   H 8.09;   N 9.36;   Cl 23.70

<u>4,5-Dimethyl-3,6-dihydro-ortho-oxazine.</u> 11.2 g of caustic potash was added gradually, with cooling, to a solution of 15.0 g (0.1 mol) of 4,5-dimethyl-3,6-dihydro-ortho-oxazine hydrochloride in 10 ml of water at 0°, the potassium chloride forming was filtered off, the filtrate was extracted with ether, and the ether extract was dried with anhydrous sodium sulfate. It contained 8.1 g (71.7% yield) of 4,5-dimethyl-3,6-dihydro-ortho-oxazine, a colorless mobile liquid, b.p. 83.5-84°/20 mm; d_4^{20} 1.0027; n_D^{20} 1.4363; found MR_D 32.42; calculated MR_D 32.46.

Found %: C 63.27; 63.26; H 9.88; 9.82; N 12.57; 12.51
$C_6H_{11}ON$. Calculated %: C 63.68;   H 9.80;   N 12.38;

The picrate of 4,5-dimethyl-3,6-dihydro-ortho-oxazine melted at 169-170° (decomposition), after recrystallization from water.
Found %: N 16.30; 16.34. C12H14O$_3$N$_4$. Calculated %: N 16.37.

<u>2-(3',5'-dinitrobenzoyl)-4,5-dimethyl-3,6-dihydro-ortho-oxazine.</u> A mixture of 0.58 g (0.0025 mol) of 3,5-dinitrobenzoyl chloride, 0.37 g (0.0025 mol) of 4,5-dimethyl-3,6-dihydro-ortho-oxazine hydrochloride, and 1 ml of dry pyridine gave 0.5 g (64.9%) of this product, m.p. 168.5°, after recrystallization from methanol.

Found %: C 50.86; 50.70; H 4.43; 4.35; N 13.61; 13.68
$C_{13}H_{13}O_6N_3$. Calculated %: C 50.81;   H 4.26;   N 13.68

<u>3,6-endoethyleno-3,6-dihydro-ortho-oxazine hydrochloride.</u> 4.0 g (0.05 mol) of cyclohexa-1,3-diene is added, cooling in ice, to a solution of 6.64 g (0.045 mol) of 1-chloro-1-nitroso-cyclohexane in 16 ml of ether and 6 ml of ethanol. The mixture was left on ice for 30 min, by which time a considerable amount of crystalline product had formed, and it was then kept at room temperature for 6 hrs, and filtered. The crystalline product was recrystallized from ethanol, giving 5.91 g (89.0%) of the salt, m.p. 147-147.5° (decomposition).

Found %: C 48.85; 48.65; H 7.01; 7.17; N 9.59; 9.56; Cl 23.97; 23.75
$C_6H_{10}ONCl$. Calculated %: C 48.82;   H 6.83;   N 9.49;   Cl 24.02

<u>3,6-endoethyleno-3,6-dihydro-ortho-oxazine.</u> 5.4 g of caustic potash was added gradually, with cooling, to a solution of 10.0 g (0.068 mol) of 3,6-endoethyleno-3,6-dihydro-ortho-oxazine hydrochloride in 6 ml of water, the precipitate of potassium chloride was filtered off, and the filtrate was extracted three times with

ether, the ethereal extract was dried with anhydrous sodium sulfate, and the ether was distilled off in vacuum, leaving a white waxy residue. This was recrystallized from cyclohexane, giving 6.60 g (87.7%) of white, waxy product, m.p. ~72°.

Found %: C 64.56; 64.62; H 8.21; 8.52
C_6H_9ON. Calculated %: C 64.84; H 8.16

The picrate of 3,6-endoethyleno-3,6-dihydro-ortho-oxazine melted at 147.5-148° (decomposition), after recrystallization from water.

Found %: N 16.59; 16.62
$C_{12}H_{12}O_8N_4$. Calculated %: N 16.47

2-Benzoyl-3,6-endoethyleno-3,6-dihydro-ortho-oxazine. 2.1 g (0.01 mol) of benzoyl chloride was added in three portions, with violent shaking, to a mixture of 1.11 g (0.01 mol) of 3,6-endoethyleno-3,6-dihydro-ortho-oxazine in 10 ml of 10% aqueous caustic soda, the precipitate was dissolved in ether, the extract was washed successively with water, 5% aqueous caustic soda, 3% hydrochloric acid, and water, the ether was distilled off, and the residue was recrystallized from ethanol, giving 1.55 g (72.1%) of product, m.p. 109°.

Found %: C 72.27; 72.34; H 6.32; 6.44; N 6.61; 6.77
$C_{13}H_{13}O_2N$. Calculated %: C 72.54; H 6.09; N 6.51

2-(3',5'-dinitrobenzoyl)-3,6-endoethyleno-3,6-dihydro-ortho-oxazine. 0.37 g (0.0025 mol) of 3,6-endoethyleno-3,6-dihydro-ortho-oxazine hydrochloride, 0.58 g (0.0025 mol), of 3,5-dinitrobenzoyl chloride, and 1 ml of dry pyridine, gave a product melting at 166.5-167° (decomposition), after recrystallization from methanol; yield 0.64 g (84.2%).

Found %: C 51.15; 51.12; H 3.81; 3.87; N 13.95; 14.10
$C_{13}H_{11}O_8N_3$. Calculated %: C 51.15; H 3.63; N 13.77

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DISCUSSION

DISTRIBUTION OF π-ELECTRON DENSITY AND INTERATOMIC DISTANCES. 2

G. V. Bykov

In my first paper on this subject [1] the basic principles of the hypothesis of π-electron distribution were presented, equations were derived for the calculation of interatomic distances and π-electron charges of bonds, and, on the example of CC and CH bonds in unsaturated and aromatic hydrocarbons, the advantages of the proposed method over other ones explaining experimental data relating to interatomic distances in these compounds, were pointed out. The present paper, which is a direct continuation of the former one, extends the π-electron distribution hypothesis to the most important of the remain-types of bonds occurring in organic compounds.

CCl, CBr, and CI bonds. The length of the σ-bond between carbon and halogen in compounds of the types CX_4 and CH_3X varies, as is known. The second type is, of course, more characteristic of organic halogen compounds. For this reason we take as standard lengths of CX bonds those determined spectroscopically in methyl chloride, iodide, and bromide, viz., $L_{CCl} = 1.779$, $L_{CBr} = 1.936$ and $L_{CI} = 2.132$. The lengths of the bonds in the corresponding dihalogenoethylenes are $l_{CCl} = 1.640$ and $l_{CC} = 1.195$; $l_{CBr} = 1.80 \pm 0.03$ and $l_{CC} = 1.20 \pm 0.03$; $l_{CI} = 2.03 \pm 0.10$ and $l_{CC} = 1.18$. The calculation of specific striction from these figures seems scarcely possible for CBr and CI bonds, although the calculated value of Δ_{CBr} is indirectly confirmed (v.i.).

For the calculation of Δ_{CX} we use formula (6), whence $\Delta_{CX} = \dfrac{L_{CX} - l_{CX}}{A_{CX}}$; according to formula (11)

$2 A_{CX} + A_{CC} = 4$, and hence

$$\Delta_{CX} = \frac{L_{CX} - l_{CX}}{2 - \dfrac{L_{CC} - l_{CC}}{2\Delta_{CC}}}$$

Calculating from this formula we obtain:

$$\Delta_{CCl} = 0.166; \quad \Delta_{CBr} = 0.16 \text{ and } \Delta_{CI} = 0.13.$$

We shall now consider certain experimental data.

The CCl bond approaches the value of the ethylenic bond in vinyl chloride ($l_{CCl} = 1.69 \pm 0.02$); isocrotyl chloride (1.72 ± 0.02); 1,2-dichloroethylene (1.69 ± 0.02, or what seems to be too low a value, 1.67 ± 0.03); 1,1-dichloroethylene (1.69 ± 0.02); trichloroethylene (1.72 ± 0.02); tetrachloroethylene (1.73 ± 0.02; 1.71 ± 0.02). The magnitude of the π-electron charge calculated from equation (8) fluctuates within the limits $A_{CCl} = 0.5 \pm 0.1 \, \pi$ (in vinyl chloride and dichloroethylenes) to $A_{CCl} = 0.3 \pm 0.1 \, \pi$ (in tetrachloroethylene), i.e., it is in all cases greater than $A_{CH} = 0.14 \, \pi$ in ethylene. The same picture is given by the chlorinated benzenes: hexachlorobenzene (1.70 ± 0.03); 1,2,4,5-tetrachlorobenzene (1.72 ± 0.04); 1,3,5-trichlorobenzene (1.69 ± 0.03); m- and p-dichlorobenzene (1.69 ± 0.03); o-dichlorobenzene (1.71 ± 0.03), and chlorobenzene (1.69 ± 0.03).

The length of the CBr bond approaches that of the ethylenic bond, in vinyl bromide (1.86 ± 0.04); dibromoethylene (1.85 ± 0.04; 1.91 ± 0.05 and 1.86 ± 0.04); and tetrabromoethylene (1.91 ± 0.05), and in aromatic compounds: 1,3,5-tribromobenzene (1.84 ± 0.02); p-dibromobenzene (1.88 ± 0.02); o-dibromobenzene (1.89); 4,5-dibromo-o-xylene (1.88 ± 0.02); 5,6-dibromodihydroindene (1.84 ± 0.02); 6,7-dibromotetralin (1.86 ± 0.02); 3,3'-dibromodiphenyl (1.88). The value of the π-electron charge of the CBr bonds varies from $A_{CBr} = 0.6 \, \pi$ to $A_{CBr} = 0.2 \, \pi$.

There are very few available figures for the CI bond, and since the determination of Δ_{CI} itself is insufficiently accurate we do not propose to analyze these figures, but shall confine ourselves to remarking that in general they are not in conflict with the assumptions that will be made further on in this paper.

The reason why the value of A_{CX} in halogen derivatives of ethylene and benzene is greater than that of A_{CH} in ethylene and benzene may in all probability be sought, within the limits of the π-electron distribution hypothesis, in the passage of π-electron charges of CC and CH bonds to CX bonds. As a result, in the series $C_2H_3X-C_2H_2X_2-C_2HX_3-C_2X_4$, the π-electron charges of CX bonds (and also of CC bonds) should diminish, and their length should increase. In general, as appears from the above-cited data, these consequences are confirmed by experiment, insofar as concerns the CX bond (sufficiently accurate data are not available for CC bonds). As applied to aromatic halogen derivatives, it follows from these conclusions that the π-electron charge of CCl bonds in the ortho-position (or generally in the vicinal position) will be smaller, and the length of the bond will be greater, than in the para- or the meta-position. The data available for chloro-derivatives are not in conflict with this conclusion.*

CO bond. In view of the lack of data for CO σ-bonds, accurate to the third decimal,** we are obliged to take the arithmetic mean of the values for the length of CO bonds in methyl ether (1.42 $\pm$ 0.03; ethanol (1.43 $\pm$ 0.02); ethylene glycol (1.43; 1.43 $\pm$ 0.02); trioxymethylene (1.42 $\pm$ 0.03; 1.46 $\pm$ 0.02); pentaerythritol (1.46 $\pm$ 0.03); paraldehyde (1.43 $\pm$ 0.02); methanol (1.44 $\pm$ 0.01); ethylene chlorohydrin (1.43); dioxyethylenemethylene (1.42 $\pm$ 0.03); methylal (1.42 $\pm$ 0.02); glycerol (1.43); tetrahydrofuran (1.43 $\pm$ 0.03); dioxan (1.46 $\pm$ 0.04; 1.42; 1.44 $\pm$ 0.03); and ethyl ether (1.43 $\pm$ 0.02). L_{CO} = 1.43.

Data for the length of the bond in carbon monoxide, l_{CO} = 1.129, in carbon dioxide, l_{CO_2} = 1.159, or, according to other estimates, l_{CO} = 1.1632, can be applied to the determination of the specific striction of the CO bond. An argument against the use of data relating to carbon dioxide is that it contains cumulated double bonds, similarly to allene, and, as will be shown later, $\Sigma S < n$ for such compounds. On the other hand, carbon monoxide is generally considered as an anomalous compound, and some authors believe that its molecule may, similarly to that of nitrogen, develop a triple bond. The closeness of the lengths of the bonds in carbon monoxide and dioxide suggests that this is a very doubtful assumption, and that, until more convincing basic data are forthcoming, carbon monoxide may be accepted as a substance with a "normal" double bond, for the purpose of calculating Δ_{CO}:

$$\Delta_{CO} = \frac{L_{CO} - l_{CO}}{A_{CO}} = \frac{1.43 - 1.13}{2} = 0.15.$$

We shall now consider certain facts relating to interatomic distances in oxygen-containing organic compounds. The length of the CO bond in ketones and aldehydes varies within narrow limits: formaldehyde (1.21 $\pm$ 0.01; 1.225); glyoxal (1.20 $\pm$ 0.01); acetaldehyde (1.22 $\pm$ 0.02); diacetyl (1.20 $\pm$ 0.02); the values for CO bonds of carboxylic acids and esters are close to these: oxalic acid (1.22; 1.20); formic acid (1.225 $\pm$ 0.02); acetic acid (1.24 $\pm$ 0.03); methyl formate (1.21 $\pm$ 0.03); methyl acetate (1.22 $\pm$ 0.03), arithmetic mean l_{CO} = 1.22 $\pm$ 0.02. According to formula (8) A_{CO} = 1.4 $\pm$ 0.1 π. The π-electron charge $A' = 2 - A_{CO} = 0.6 \pm 0.1 \pi$ is shared between two CC bonds (in ketones), and between CC and CH bonds (in aldehydes), between CH and CO bonds (in formic acid or its esters), and between CC and CO bonds (in other carboxylic acids and their esters). As may, however, be concluded from interatomic distances, competition between CO and CH or CC bonds leads to practically the whole of the charge A' being transferred to the CO bond. The length of the simple CO bond in these compounds, as calculated from formula (7), should then have the limiting value l_{CO} = 1.34. In fact, the length of the CO hydroxyl bond of formic acid is (1.368 $\pm$ 0.03); of methyl formate (1.36 $\pm$ 0.04); and of methyl acetate (1.36 $\pm$ 0.04). This obliges us to regard the determinations of the length of the CO hydroxyl bond in acetic acid (l_{CO} = 1.43 $\pm$ 0.03) with some doubt.

Transfer of most of the π-electron charge A' to the CO bond is also observed when this bond is vicinal to an ethylenic, instead of a carbonyl bond. Thus in vinyl ether l_{CO} = 1.40 $\pm$ 0.03 and l_{CC} = 1.34 $\pm$ 0.03; in furan l_{CO} = 1.40 $\pm$ 0.02; and in dioxadiene l_{CO} = 1.41 $\pm$ 0.03; and since $2A_{CH}$ = 0.28 π for ethylene [1], it follows from formula (7) that l_{CO} = 1.43 $-$ 0.28 $-$ 0.15 = 1.39, for the limiting case of transfer of the whole of the π-electron

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* Only in hexachlorobenzene is the greatest length of the CCl bond to be expected. The determination of the length of the CC bonds of this compound would be of particular interest; it should exceed that of CC bonds of other halogen derivatives of benzene.

** It is true that the length of the CO bond of ethylene oxide, as determined spectroscopically, is l_{CO} = 1.4363, but the length of the CC bond of this compound, l_{CC} = 1.4728, is anomalous, which puts the "standardness" of the CO bond in question.

charge from the CH to the CO bond.

Competition between CH and CC bonds in aldehydes is not so strenuous, and for this reason, assuming that for each bond neighboring with a carbonyl one in aldehydes (and ketones) $A'/2 = 0.3\,\pi$, we obtain from formula (7) $l_{CC} = 1.50$, whereas the experimental value for acetaldehyde is $l_{CC} = 1.50 \pm 0.02$.* This explains the fact, which was inexplicable to Welland [2], that shortening of CC bonds occurs when they neighbor on carbonyl bonds, but is absent when they are next to an ethylenic bond.

The shortening of the central CC bonds of glyoxal and diacetyl should be at least twice as great as in acetaldehyde, where $l_{CC} = 1.50 \pm 0.02$. Assuming, however, that as with butadiene [1] the presence of "counter-current" π-charges causes increase in the π-electron charge of the central bond, at the expense of the vicinal ones (this is confirmed by the finding that the value of l_{CC} is 1.54 ± 0.02 for the CH_3-C bond of diacetyl), we calculate the length of the central bond of diacetyl as being $l_{CC} = 1.40$, whereas the experimental value is $l_{CC} = 1.47 \pm 0.02$. We evidently have here the repulsive effect mutually exerted by the carbonyl groups, which opposes the shortening of the CC bond in glyoxal and diacetyl, and even leads to the lengthening of the CC bond in oxalic acid ($l_{CC} = 1.57; 1.59$). Where there is no electrostatic repulsion, as in benzoquinone ($l_{CC} = 1.50; l_{C=C} = 1.32$ and $l_{CO} = 1.14$), there is no anomaly; $S_{CC} + S_{CO} = .8\,\pi$.

Of the scanty data available for polyhydric phenols resorcinol $l_{CO} = 1.36; 1.37$ and $l_{CC} = 1.39 \pm 0.01$ and phloroglucinol $l_{CO} = 1.36$ and $l_{CC} = 1.40$ it seems questionable that the length of the CC bond should remain unchanged, the more so as $A_{CO} = 0.5\,\pi$, as calculated from formula (8).

Formula (11) is not applicable to oxygen-containing compounds with cumulated bonds, similarly to allene. For example, for carbon suboxide ($l_{CO} = 1.20 \pm 0.02$ and $l_{CC} = 1.29 \pm 0.03$) $\Sigma S = 6.4 \pm 0.7\,\pi$ instead of 8π. For keten $H_2C \equiv C \equiv O$ ($l_{CO} = 1.102$ and $l_{CC} = 1.353$) $\Sigma S = 3.75\,\pi$ instead of $4\,\pi$, assuming that $2A_{CH} = 0.28\,\pi$, as in ethylene and allene. Finally, in the carbonate ion ($l_{CO} = 1.23$),** assuming that its structure is represented by

the formula ![carbonate structure], $3A_{CO} = 4\pi$, instead of 6π. The length of the bond may here be affected by mutual repulsion of oxygen atoms, as the carbonate ion may be regarded as three carbonyl groups having a common carbon atom.

The postulates and methods of calculation presented above can also be extended to oxygen-containing organic compounds containing other elements in addition to carbon and hydrogen. Thus, for methyl chlorocarbonate ($l_{CCl} = 1.74 \pm 0.02; l_{CO} = 1.19 \pm 0.03$ and $l_{CO'} = 1.35 \pm 0.04$) $A_{CCl} + A_{CO} + A_{CO'} = 2.4\pi$. For phosgene ($l_{CCl} = 1.74 \pm 0.02$ and $l_{CO} = 1.18 \pm 0.03$) $\Sigma S = 2.1\,\pi$; other data are available for phosgene ($l_{CCl} = 1.68 \pm 0.02$ and $l_{CO} = 1.23 \pm 0.02$), but they lead to practically the same value of $\Sigma S = 2.2\,\pi$, as if the authors of the corresponding papers had been dealing with two electron isomers of phosgene.

CN bond. Similarly as for the CO bond, the standard length of the CN bond was taken as the arithmetic mean of the values of l_{CN} for trimethylamine ($1.47 \pm 0.02; 1.47 \pm 0.01$); hexamethylenetetramine ($1.47 \pm 0.02; 1.48 \pm 0.01$); methylamine ($1.47 \pm 0.01; 1.48$); N-chlorodimethylamine (1.47 ± 0.02); dimethylamine ($1.46 \pm 0.03; 1.47 \pm 0.02$); ethylamine ($1.47 \pm 0.02$), triethylamine ($1.47 \pm 0.02$); and dimethylhydrazine (1.47 ± 0.03). $l_{CN} = 1.47$.

Calculation of specific striction of the CN bond from the data for HCN ($l_{CN} = 1.154$ and $l_{CH} = 1.057$), BrCN ($l_{CN} = 1.158$ and $l_{CBr} = 1.790$) and ClCN ($l_{CN} = 1.163$ and $l_{CCl} = 1.629$) by the formula

$$\Delta_{CN} = \frac{l_{CN} - J_{CN}}{4 - \dfrac{l_{CX} - l_{CX}}{\Delta_{CX}}}$$

leads to one and the same value for $\Delta_{CN} = 0.10$, which testifies to the good mutual

* The data for acetone, $l_{CO} = 1.14$ and $l_{CC} = 1.56$, appear very unreliable, in view of this.

** Although the original paper [3] quoted three values for l_{CO} in the carbonate ion ($l_{CO} = 1.23 \pm 0.02; 1.23 \pm 0.02$ and 1.26 ± 0.02), it will involve no great error if we take all three as being equal to 1.23, since the calculation of l_{CO} for this ion is only for the purpose of illustration, and also as the value $l_{CO} = 1.26$ applies to a CO bond of which the oxygen takes part in a hydrogen bridge. The fact that lengthening of the bond takes place, with consequent diminution of its π-electron charge as a consequence of participation of its oxygen in a hydrogen bond, is evidence in favor of the π-electron nature of the latter.

agreement of the numerical values for the specific striction of the CC, CH, CBr, and CCl bonds.

Although much more diversity is to be found in the types of bonds of nitrogen-containing than of oxygen-containing compounds, data relating to their interatomic distances are far more scanty. Calculation of the π-electron charge of the CN bond in hydrogen cyanide and cyanogen bromide and chloride, using equation (8), and taking $l_{CN} = 1.16$, gives $A_{CN} = 3.1\,\pi$. Equation (11) is inapplicable to a number of compounds with the cyanide bond. In methyl cyanide ($l_{CC} = 1.49 \pm 0.03$ and $l_{CN} = 1.16 \pm 0.03$) $A_{CC} + A_{CN} = 3.4\,\pi$ instead of $4\,\pi$, but it may here be supposed that, as in the case of dimethyldiacetylene [1], the CH bonds of the methyl group, for the length of which no data are available, also possess certain electron charges. For cyanogen ($l_{CC} = 1.37 \pm 0.02$ and $l_{CN} = 1.16 \pm 0.02$) $\Sigma S = 7.4 \pm 0.5\,\pi$, instead of $8\,\pi$, and for hydrogen cyanate ($l_{CN} = 1.19 \pm 0.03$ and $l_{CO} = 1.19 \pm 0.03$) $A_{CN} + A_{CO} = 4.4 \pm 0.5\,\pi$ instead of $4\,\pi$. The experimental data obviously require further more accurate work.

Calculation shows that for methyl isocyanide CH_3-N-C^* ($l_{CN} = 1.426$ and $l_{C^*N} = 1.167$) $A_{CN} = 0.4\,\pi$ and $A_{C^*N} = 3.0\,\pi$, and this is further evidence that the C*N bond is closer to a triple than to a double bond, i.e., that methyl isocyanide corresponds not with the formula $CH_3-N\cdot\cdot C$, but with the formula $CH_3-N\vdots C$. In methyl isocyanate CH_3-N-C^*-O $l_{C^*N} = 1.19 \pm 0.03$ and $l_{C^*O} = 1.18 \pm 0.03$. Assuming that, as for methyl isocyanide, $l_{CN} = 1.43$, we obtain $A_{C^*N} + A_{CN} + A_{CO} = 4.9 + 0.5\,\pi$ instead of $4\,\pi$; apart from this, we have here a cumulation of double bonds, which led in the above examples to diminution in the value of ΣS. It is evident that in the given case there are grounds for considering the C*N bond a triple one, and for writing the formula of methyl isocyanate as $CH_3-N\vdots C-O$.

It is probable that the same concept, involving cumulated bonds, applies also to urea ($l_{CN} = 1.37$ and $l_{CO} = 1.25$), in which $A_{CN} = 1.0\,\pi$ and $A_{CO} = 1.2\,\pi$ and, consequently, $2A_{CN} + A_{CO} = 3.2\,\pi$ instead of $2\,\pi$. The assumption that the π-electron charge of the CN bond of urea is augmented at the expense of unshared electron pairs of nitrogen seems for this reason to be a quite natural one, and a structure of urea involving symmetrical distribution of π-electron charges to a certain extent resembles that of the carbonate ion. The full or partial (possibly proportional to "counter-current" π-electron charges) participation of unshared electron pairs in forming π-electron charges of individual bonds is a conclusion strongly supported by experimental facts. We shall below present fresh examples, relating to nitrogen, for which this phenomenon is especially characteristic, although it also applies to oxygen (as in the case of polyhydric phenols). It is not so clear whether unshared electron pairs of halogens can contribute to π-electron charges of bonds.

The π-electron charge in pyridine ($l_{CN} = 1.37 \pm 0.03$) is $A_{CN} = 1.0 \pm 0.3\,\pi$, and in pyrazine ($l_{CN} = 1.35 \pm 0.02$) $A_{CN} = 1.2 \pm 0.2\,\pi$; this is still further evidence of the structural similarity of these compounds to benzene.

Acetamide and pyrrole are typical examples of compounds in which the CN bond is next to a multiple bond. In acetamide ($l_{CC} = 1.51 \pm 0.05$; $l_{CN} = 1.38 \pm 0.05$ and $l_{CO} = 1.28 \pm 0.05$) $A_{CC} + A_{CN} + A_{CO} = 2.1\,\pi$. In the same way as in acids the π-electron charge is distributed asymmetrically between CC and CO bonds which are next to carbonyl bonds, so in acetamide the greater part of the charge undergoes transfer to the CN bond ($A_{CN} = 0.9\,\pi$; $A_{CC} = 0.2\,\pi$). In pyrrole ($l_{CN} = 1.42 \pm 0.02$) $A_{CN} = 0.5\,\pi$. If we calculate the length of the CN bond, as was done before, we obtain the value $l_{CN} = 1.47 - 0.28 \cdot 0.10 = 1.44$.

In glycine ($l_{CN} = 1.39 \pm 0.2$) $A_{CN} = 0.8\,\pi$ and in alanine ($l_{CN} = 1.42 \pm 0.03$) $A_{CN} = 0.5\,\pi$. Before attempting to explain this we should be in possession of more reliable data for the lengths of the CN, CC, and both CO bonds. There are unfortunately no data whatsoever for amino- and nitro-derivatives of benzene from which the drawing of any conclusions could be possible.

N N bond. We have no data justifying the acceptance of any particular length of the σ-bond as a standard one; in hydrazine ($l_{NN} = 1.47 \pm 0.02$) and in dimethylhydrazine ($l_{NN} = 1.45 \pm 0.02$), from which the arithmetic mean $L_{NN} = 1.46$. Spectroscopic determination of the length of the bond in the nitrogen molecule $N\vdots N$ $l_{NN} = 1.095 \pm 0.008$ and 1.098, or, in round figures, $l_{NN} = 1.10$.

$$\Delta_{NN} = \frac{1.46 - 1.10}{4} = 0.09.$$

In methyl azide $H_3C-\ddot{N}-N\vdots N^*$ ($l_{CN} = 1.47 \pm 0.02$; $l_{NN} = 1.24 \pm 0.02$; 1.26 ± 0.02 and $l_{NN^*} = 1.10 \pm 0.02$) $A_{CN} = 0.0$; $A_{NN} = 2.3\,\pi$ and $A_{NN^*} = 4\,\pi$, whence $S_{NN} = 6.3\,\pi$, while $n = 6\,\pi$. In hydrazoic acid ($l_{NN^*} = 1.128$ and $l_{NN} = 1.241$) $S_{NN} = A_{NN} + A_{NN^*} = 2.4 + 3.7 = 6.1\,\pi$. In diazomethane $H_2C-N\vdots N$ ($l_{CN} = 1.34$ and $l_{NN} = 1.13$),

$A_{CN} + A_{NN} = 5\pi$, while $n = 6\pi$. It is evident that the CH bonds of this compound have undergone considerable shortening.

In azobenzenes ($l_{NN} = 1.23 \pm 0.03$ and $l_{CN} = 1.40; 1.40; 1.43$) $A_{NN} = 2.6\pi$ and (for an arithmetic mean $l_{CN} = 1.41$) $A_{CN} = 0.6\pi$. These results give an indication that the azo-group has the structure $-N\overset{..}{=}N-$ and hence that an unshared pair (or pairs) of nitrogen electrons participate in the bonds. However, in azomethane ($l_{NN} = 1.24 \pm 0.05$ and $l_{CN} = 1.47 \pm 0.06$) $A_{NN} = 2.4\pi$, and $A_{CN} = 0.0$. Incidentally, these rather old results require checking.
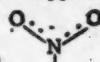
TABLE

Bond	L	Δ	A
CC	1.542	0.149	+0.07
CH	1.093	0.042	+0.24
CCl	1.779	0.166	+0.06
CBr	1.936	0.16	+0.06
CI	2.132	0.13	+0.08
CO	1.43	0.15	+0.07
CN	1.47	0.10	+0.10
NN	1.46	0.09	+0.11
NO	1.37	0.08	+0.12

NO bond. In the absence of other values the standard length of the NO bond is taken as being that in O-methylhydroxylamine, $L_{NO} = 1.37$. Specific striction of this bond may also be very roughly derived from $l_{NO} = 1.22 \pm 0.02$ in methyl nitrite, since the other NO' and the CO' bonds have the normal values $l_{NO'} = 1.37 \pm 0.02$ and $l_{CO'} = 1.44 \pm 0.02$:

$$\Delta_{NO} = \frac{1.37 - 1.22}{2} = 0.08.$$

Since the length of the CO bond in nitromethane ($l_{NO} = 1.22 \pm 0.02$); methyl nitrate (according to more recent data also 1.22 ± 0.04); and tetranitromethane (1.22 $+ 0.02$) is identical with that in methyl nitrite, it is natural to suppose that the structure of the nitro-group is expressed by the formula, and hence that "unshared" electron pairs of nitro-compounds donated by nitrogen participate fully in making up the π-bonds.

Equation (11) is fully satisfied for nitrous oxide ($l_{NN} = 1.126$ and $l_{NO} = 1.191$) $A_{NN} + A_{NO} = 5.95\pi$, whereas in accordance with the formula $N\overset{..}{=}N-O$ $n = 6\pi$.
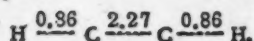
The anomalous length of the bond in trimethylamine oxide ($l_{NO} = 1.44 \pm 0.04$ at $l_{CN} = 1.49 \pm 0.02$; according to older data $l_{NO} = 1.36 \pm 0.03$ and $l_{CN} = 1.54 \pm 0.03$) may be explained as being due to the special ("semipolar") nature of the NO bond in this compound. •

The hypothesis of π-electron distribution thus allows us to combine together and consider from a single point of view the data for interatomic distances in compounds with multiple bonds. In spite of the apparently large amount of such material available, there are serious gaps in the coverage of benzene derivatives (in particular of monosubstituted ones) and of compounds containing nitrogen and iodine, and there are practically no trustworthy data relating to CH bonds. Thus we see that this mass of data was accumulated in a most haphazard manner; one of the virtues of the hypothesis presented by us is that it can be applied to the solution of a number of problems, and can also suggest experimental approaches towards the solution of new problems in the field of interatomic distances, which are of great theoretical importance, and which are ultimately concerned with the elucidation of the electron structure of molecules. In order, however, to assess correctly the cognitive possibilities inherent in the π-electron distribution hypothesis in its present stage, being the initial stage of its development, it is necessary to have a clear picture of the assumptions on which it rests, of the reliability of the basic data, and of the accuracy of the final results of the calculations.
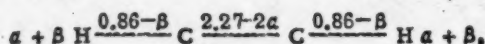
Equation (11) $\Sigma S = n$ may be called an equation of additivity of π-electron charges. If it is satisfied for a compound possessing different types of bonds, such as phosgene or nitrous oxide, or if agreement is obtained for the calculation of specific striction of the CN bond, using this equation, from different independent data, then this should be regarded as being evidence in favor of the truth of the initial hypothesis and of the correctness of the constants L and Δ. Verification of the correctness of equation (11) is unfortunately not possible for a large number of compounds, owing to the absence of data for the CH bond. Cases are, however, encountered in which equation (11) is quite obviously not satisfied (for example, compounds with cumulated multiple bonds $\overset{..}{=}C\overset{..}{=}$). The reason is that in establishing a direct proportionality between the magnitude of the π-electron charge and of striction of the bond we deliberately ignored such factors as mutual reactions of π-electrons belonging to one and the same atom, which cannot as yet be considered quantitatively, as well as irregular distribution of π-electron density along the bond, etc. We thus started with the assumption that the basic factor affecting striction of a bond is the magnitude of its π-electron charge, and that all other factors are of only secondary importance. We also postulated that the π-electron charge is confined to the limits of a bond, and that they are distributed in the

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• The values for L and Δ for various types of bonds are reported in the Table in which are reported as well as the values of ϵ_A —the absolute errors in the determination of the π-electron charge, if the absolute error in the determination of the bond length $\epsilon_l = \pm 0.01$.

following way in acetylene:

$$H \xrightarrow{0.36} C \xrightarrow{2.27} C \xrightarrow{0.86} H,$$

but not, for example, as follows:

$$a + \beta \; H \xrightarrow{0.86-\beta} C \xrightarrow{2.27-2a} C \xrightarrow{0.86-\beta} H \; a + \beta,$$

where a and β are fractions of a π-electron charge, or, at least, that these fractions are so small as to be negligible for the purposes of our calculation. The agreement of most of the data for interatomic distances with the π-electron distribution hypothesis is evidence in favor of the above assumption. The existing exceptions do not invalidate this assumption, since they themselves may in turn be generalized, as in the case of compounds with cumulated multiple bonds, or they may even be explained, in some cases. Thus the greater length of the central bonds than the calculated values, observed in the cases of oxalic acid, glyoxal, and diacetyl, is explained as being due to the mutual electrostatic repulsion of carboxylic and carbonyl groups, and the greater observed than calculated striction of bonds in isocyanides, isocyanates, and certain other compounds, to partial participation of unshared electron pairs in the formation of the π-electron cloud of these bonds. In some cases the experimental data on which apparent exceptions are based may be questioned, such as the interatomic distances in acetone, the length of the hydroxyl bond of CO in acetic acid, the length of the CH_3-C bond in p-xylene, etc.

A reason for the discordance of certain data, and the non-applicability of equation (11) may also be a result of inaccuracies in the results calculated from equations (8) to (10) for π-electron charges, and this, in turn, is a result of inaccuracies in the determination of the magnitudes entering into these equations, such as the experimental values for the length of a bond l, the standard length of the σ-bond L, and the specific striction Δ. We shall therefore consider the effect of inaccuracies in the determination of each of these magnitudes on the result of calculation of the π-electron charge A by equation (8).

1. Interatomic distances are determined spectroscopically with an absolute error of the order of thousandths of an Angstrom, but these methods are applicable only to the simplest molecules. The authors of papers on determination of interatomic distances by roentgenographic and electronographic methods estimate the absolute error involved at $\epsilon_1 = \pm 0.02, \pm 0.03$ and even ± 0.04. In most cases, however, the absolute error indicated in the tables is on the high side, and, in fact, of the nineteen above-quoted values for the length of the unexcited CO σ-bond, as found for a number of compounds, calculations based on the formulas of the theory of mean errors give as the probable error of an individual determination a value of $\eta_{CO} = \pm 0.009$. As regards the absolute ϵ_A and the relative δ_A of errors of determination of the π-electron charge, it follows from equation (8) that

$$\epsilon_A = \pm \frac{\epsilon_1}{\Delta}, \quad \text{while} \quad \delta_A = \pm \frac{\epsilon_1}{\Delta A} \cdot 100\%.$$

It is evident from the above Table, which gives ϵ_A values calculated on the assumption that $\epsilon_1 = \pm 0.01$, that the determination of the length of the CH bond has to be performed with particular accuracy. Inasmuch as we possess as yet only isolated measurements of interatomic distances for the vast majority of organic compounds, and hence cannot subject these to the usual mathematical treatment, it is reasonable to take into consideration not the values of absolute errors as given by the authors of the appropriate papers, but the correspondence of data obtained for bonds of one and the same type in structurally analogous members of a series of compounds.

2. For the standard length L of the σ-bond we have taken either the arithmetic mean of a series of values for the lengths of bonds of one and the same type in compounds not possessing multiple bonds, or else we have taken single determinations, usually obtained by the spectroscopic method. The values of L were derived by the former method for CO, CN and NN bonds, and in these cases it is possible to calculate the probable error η_L of the arithmetic mean. We obtained the value $L_{CO} = 1.430 \pm 0.002$ for the CO bond, from the above-cited data, but since, as has been shown above, the probable error of each separate determination of bond length for CO would be $\eta_1 = \pm 0.009$, it follows that the value of L_{CO} should be taken only to the second decimal place. For the NN bond we were obliged to take the arithmetic mean of two determinations only.

Experimental values for the CC, CH, CCl, CBr, CI, and NO bonds were taken for L, by the second method. Here too we took into consideration the arithmetic means, which, for example, coincide for the CC bond with $l_{CC} = 1.542$ in diamond (roentgenographic method), but not with $l_{CC} = 1.573$ in ethane (spectroscopic method).

It should not, strictly speaking, be considered that any given value of L could serve as a standard for σ-bonds of all compounds. Thus the length of the CC σ-bond is different in ethane and in hexachloroethane, and it was hence necessary, in calculating the π-electron charge of ethylene and tetrachloroethylene, to take different values for L_{CC}. In view, however, of the insufficient trustworthiness of the relevant experimental data, and of the absence of even semi-quantitative generalizations relating to the relatively small fluctuations in the length of the σ-bond in saturated compounds, it seemed to me that it would be premature to attempt to introduce the corresponding corrections.

All that we said above regarding inaccuracies in the determination of the length l of bonds applies equally to the effect of errors made in determining L on the result of calculating the π-electron charge A.

3. Specific striction Δ can be either calculated independently, as has been done above for the CO and NN bonds, or else, as in most cases, it can be derived from equation (11), as for CC and CH bonds [1]. Calculation of Δ_{CCl}, Δ_{CBr} and Δ_{CI} was made by means of equations containing the terms Δ_{CC} and Δ_{CN}, from equations containing the terms Δ_{CH}, Δ_{CBr} or Δ_{CCl}. Whichever method of calculation is used, the trustworthiness of the values for the standard length L of the σ-bond and of the experimentally determined values l of bond length are of great importance for the calculation of specific striction. The value of l is selected from individual results (mostly spectroscopic) for simpler compounds (acetylene, ethylene, dichloro-, dibromo-, and diiodo-ethylene, carbon monoxide, hydrogen cyanide, etc). As has already been said, the selection of carbon monoxide for calculation of Δ_{CO} cannot be accepted without reservation. Inaccuracies in the determination of data for ethylene, in particular for its CH bond,* may be the most serious source of error in calculating specific striction of a whole series of bonds, since any such inaccuracies are multiplied by 4 in the process of calculation.

Without doubt sufficiently trustworthy values will with time be available for l, L, and Δ, but until then the values calculated from equations (8) to (10) can only be regarded as giving a semi-quantitative, or even only a qualitative, picture of distribution of π-electron density among the bonds of organic compounds. It will in time be possible to define more narrowly the limits of applicability of the basic hypothesis, and to explain the observed deviations from them. Even now, however, the π-electron distribution hypothesis can be applied to the explanation or even to the calculation of certain properties, chiefly additive ones, of organic compounds, giving additional quantitative material relating to distribution of π-electron charges on different types of bonds in molecules; as will be shown by me in future papers this possibility is quite a real one. The π-electron distribution hypothesis thus promises to become a step forward towards the formulation of a semi-quantitative theory of the electron structure of chemical compounds. Further steps along this path will be the study of the relation between the π-electron density distribution and the physical properties of a substance, the application of the methods elaborated to the study of σ-electron density distribution, the establishment of the laws governing reaction and mutual transformation of π- and σ-electron densities, the elucidation of the electron mechanism of mutual reactions between atoms, and the broader understanding of the chemical properties of molecules.

SUMMARY

1. The π-electron distribution hypothesis has been extended to organic compounds containing the CCl, CBr, CI, CO, CN, NN and NO bonds.

2. The reliability of the basic data and of the final calculated results for π-electron charges of bonds are discussed.

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* Apart from the values (l_{CC} = 1.330 and l_{CH} = 1.087), used for the calculation of Δ_{CC} and Δ_{CH} [1], we also have other data for this compound (l_{CC} = 1.353 and l_{CH} = 1.071), which we do not take into consideration, since calculation of specific striction in the way applied in our first paper leads to obtaining negative values of Δ_{CH}, which is obviously absurd.

CHRONICLE

240TH ANNIVERSARY OF THE BIRTH OF M. V. LOMONOSOV

The Division of Chemical Sciences, Academy of Sciences USSR, held a session on the 27th of November, 1951, in honor of the 240th anniversary of the birth of that great thinker and propangandist, the brilliant founder of Russian science, Mikhail Vasilievich Lomonosov.

Opening the session, Academician-Secretary of the Division of Chemical Sciences of the Academy of Sciences USSR, Academician M. M. Dubinin said: "The Soviet Union looks back with pride at the path traversed by Russian science from Lomonosov's time to the present day. This path was marked by great discoveries and achievements. Lomonosov's scientific heritage is many-sided, for he preceded the development of progressive natural scientific thought of our era. Russian chemical science has progressed to its present great successes from Lomonosov through the great chemist Butlerov and the founder of the periodic system, Mendeleev. . To Lomonosov we can trace the origin of physics, chemistry, mineralogy, geography, astronomy, metallurgy, linguistics, and literature".

Academician Dubinin pointed out that Lomonosov, by raising Russian science to the summits of knowledge, thereby raised the honor and glory of the Russian nation to an unattainable level. His genius, his devotion to his country and his nation, his uncompromising attitude towards the enemies of Russia, and his untiring energy are to us citizens of the great Soviet Union a great and inspiring example of endeavor for the good of our Fatherland.

Academician A. V. Topchiev said in his lecture: "M. V. Lomonosov — the great Russian Scientist", the creative work of M. V. Lomonosov provides striking evidence of the genius of the Russian nation, which has achieved its full development during the Stalin epoch. Lomonosov's character was influenced by his Russian national milieu, by the way in which the country itself was then developing, by the special peculiarities of the technical and social development of North Russia, which had not known the Tartar yoke or the oppression of the nobles.

Lomonosov's life-story is one of unremitting struggle for possession of knowledge, for the approach of knowledge to objective, absolute truth, against a clique of enemies of Russian science, against bureaucratic control of the Academy of Sciences, against the adoption of a servile attitude towards foreigners, against the depreciation of Russian science. His one regret, when on his death bed, was that he had not been able to achieve all that he had undertaken for the good of his country, and that with him would perish all his useful projects.

"But", continued A. V. Topchiev, "Lomonosov's useful projects did not perish. His brilliant concepts, ideas, and discoveries have become the basis of present-day science. The ideas of the conservation of mass and of energy, of atomistics, of the origin of the world and of the universe expressed by Lomonosov two centuries ago are the basic ideas of modern physics, chemistry, and geology".

The diversity of Lomonosov's work was so great that his Western contemporaries who read his odes and poems, and his scientific works on astronomy, geography, and metallurgy were convinced that these were produced by different authors. S. I. Vavilov wrote the following in a paper describing the diversity of Lomonosov's creative thought: "The great Russian encyclopedist had in fact a coherent and monolithic nature". Lomonosov was the most prominent materialist philosopher of his period. His materialistic views formed the basis of all his naturalistic papers.

Lomonosov's first scientific works, written in 1741-1746, and in particular his letters to Euler, contained the clearly expressed ideas of the conservation of mass and motion. S. I. Vavilov wrote in his articles on Lomonosov that "Lomonosov was a century ahead (of his contemporaries) in bracketing, as it were, all forms of conservation of properties of matter, the most profound content of the great natural law. . ." It was in Lomonosov's works that the idea of conservation of mass was first announced, with exceptional clarity, and was made the basis of the elucidation of the most important physico-chemical problems. A. V. Topchiev regards the

creation of the fundaments of scientific atomistics as being one of the great scientific advances due to Lomonosov.

"Lomonosov was the first of the thinkers of his time", continues A. V. Topchiev, "to form a consistent picture of nature, based on atomistic principles, and he creatively applied atomistic concepts to the solution of the most important problems of science — to the structure of substances, to the discovery of the nature of chemical reactions, and to the analysis of the laws of heat, of atmospheric electricity, etc."

Lomonosov believed that bodies consisted of corpuscles, which in turn contain a certain number of "elements", "insensitive particles". Lomonosov's "corpuscles" are molecules, and his "elements" or "insensitive particles" are the atoms of modern chemistry. Lomonosov's chemical atomistics were the foundation of all his gigantic theoretical and experimental work, which initiated the basic trends of modern scientific chemistry.

His physical researches were all connected basically with atomistics, from which standpoint he approached the problems of heat, gravity, light, and electricity. He combined brilliantly a talent for experimentation with a capacity for profound theoretical thought. He was the founder of Russian natural history. The chemical laboratory founded by him in the Academy of Sciences was a first class research establishment, and in it he created and developed a new science — physical chemistry, which followed from his atomistic views. He wrote: "Physical chemistry is a science which explains, on the basis of physical concepts and experiments, processes taking place in mixed bodies by means of chemical operations"; and, further, that he wished to "investigate all that can be measured, weighed, or determined by calculation". Lomonosov's experimental work led him to the law of the conservation of matter; this discovery has for long been credited to Lavoisier, who, however, only repeated Lomonosov's experiment 17 years later, without drawing the necessary conclusion from the result. Soviet research workers have shown that the priority for this discovery belongs properly to Lomonosov, with whose work Lavoisier was acquainted, and, further, that Lavoisier did not in his publications usually refer to the original sources.

Lomonosov's talents were many-sided, and his activities were most diversified. His chemical researches were closely connected with the Russian mosaic industry. His ideas, and his powerful urge towards practical work found their expression in geological work, in prospecting for and utilization of the limitless mineral wealth of Russia, in the study of the geography of Russia, in plans for the conquest of the Arctic, and in the organization of Arctic expeditions. Lomonosov's astronomical works combine practical application with breadth of philosophical generalizations. "Lomonosov's poetry", continued Topchiev, "is immortal, for the profundity and boldness of its scientific ideas, for its merciless opposition to reactionary forces, and for its patriotic love of his Fatherland".

Lomonosov endeavored in his poetry to inculcate a new attitude towards science, as well as to popularize new ideas throughout Russia. Before his time there was no grammar, no one took any interest in stylistic purity. Having come to the conclusion that the latter depends above all on "a thorough knowledge of the language", he undertook the compilation of his "Russian Grammar". This was the first really scientific work on the Russian language; its role was of particular interest in the light of Stalin's brilliant works on linguistics. The heritage of Lomonosov is indeed a great one; all his work was permeated by patriotism, by love for his country. The Soviet people honor the memory of the great men of the past, who under difficult conditions created the scientific and artistic treasures of the nation.

Professor N. A. Figurovsky then read a paper on Lomonosov's chemical works, and on their significance for the development of science. He said that it was only with the beginning of the present century that proper interest began to be taken in Lomonosov as a scientist, although Russian scholars, men of letters, and philologists had for two centuries studied with profound interest the personality of this remarkable man. Most of the materials relating to the activities of Lomonosov have now been published, but the study of his work, his role as the founder of science in our country, is only now beginning. His ideas and theories have inspired many important trends in the development of chemistry at least a century before they materialized. Lomonosov's slogan: "A real chemist must be a theoretician and a practical man" is particularly well understood and valued by Soviet scientists, who are participants in the great public works of Communism.

M. V. Lomonosov — atomist and research worker. His atomistics was at the core of all his theories; as a real revolutionary of science he made use of every possibility, he drew logical conclusions, and gave explanations of the most varied phenomena. In his thesis: "Elements of mathematical chemistry" he first gave his definition of chemistry, as the science relating to changes taking place in compound bodies, starting from the proposition that in "mixed bodies" (i.e., compound ones) all changes depend on changes in their internal qualities. The factors determining the internal qualities resided, in his opinion, in the properties of the particles of which the bodies are made. All bodies consist of atoms, which were then called elements. "An element is a part of a

body not consisting of any other smaller bodies which differ from it". Aggregations of elements were called "corpuscles" — in modern terminology, molecules. Lomonosov distinguished between homogeneous and heterogeneous corpuscles; "corpuscles are homogeneous if they consist of identical numbers of identical elements, joined to each other in the same way", wrote Lomonosov. "Corpuscles are heterogeneous when their elements are different, and are present in different numbers and are joined to each other differently; on this depends the infinite diversity of bodies." No one had before Lomonosov so definitely spoken of the existence of molecules of simple substances. The incorrect formulae assigned in the first half of the 19th century were due to lack of clarity regarding the nature of molecules of simple substances. The most complete confusion reigned regarding the concepts: atom, atomic weight, molecule, molecular weight, equivalent. It was not until 1860 that an international conference established order in the domain of precise definition of concepts and views first expressed by Lomonosov in 1741. Thus Lomonosov formulated the basic postulates of the atomic-molecular teaching 120 years before they were officially acknowledged.

Lomonosov realized the importance to science of the atomic theory at a time when even to dream of its direct proof was impossible. In his paper "Attempt at a theory of insensitive particles of bodies and in general of causes of qualities" certain aspects of the atomic-molecular theory are discussed in detail and extended, with particular respect to the mutual attraction of insensitive particles, and to the presence within them of forces of inertia.

Lomonosov's work "Thoughts on the causes of heat and cold" was a further step forward towards the development of progressive materialistic thinking. At a time when belief in fire material — "imponderable fluids" — was prevalent, Lomonosov took the unusual viewpoint for his times that "An adequate basis for heat is to be found in motion.....And since motion cannot exist without matter, it follows that the basis of heat is to be found in the motion of some material": He puts this more precisely as follows: "heat consists in the internal motion of matter". Thus we see that Lomonosov made an important logical conclusion as to the nature of heat, based on his atomic-molecular theory.

Lomonosov may be said to have formulated the fundaments of the molecular-kinetic theory. He postulated the existence of the absolute zero of temperature, as well as the absence of an upper limit of temperature. He repeated Boyle's experiments on the calcination of tin and lead, and demonstrated the importance of air in these experiments. His conclusions as to the mechanical theory of heat are of interest, as are those relating to phenomena of heat exchange between heated bodies: "... a cold body B immersed in a substance A can obviously not acquire a greater degree of heat than that which A has". This paper created a sensation among the ignorant foreign academicians.

Lomonosov explains, in a letter to Euler, that matter is inseparable from motion, and further develops his law of the conservation of matter and energy. The idea of the conservation of force and motion is a logical consequence of the whole complex of materialistic world outlook adopted by Lomonosov. His law is no chance remark — it is an essential part of his natural philosophy, an indispensable link of his scientific materialistic system. N. A. Figurovsky points out that it is to Lomonosov that we owe the discovery of those two great laws of nature, the law of conservation of matter and the law of conservation of energy.

Lomonosov's words resound with exceptional strength in the wonderful epoch of Stalin: "Chemistry spreads her arms widely over the affairs of men. Wherever we look, wherever we turn, we see before our eyes evidence of its successful application". Our primary task is to develop the successful applications and achievements of chemistry.

Corresponding Member of the Academy of Sciences I. N. Plaksin, in his address on "M. V. Lomonosov — founder of scientific metallurgy", spoke of the Russian "ore-experts", "prospectors", "miners", and "smiths" who laid the foundations for the further development of Russian ore mining and metallurgical industries, the inception of which belongs to a remote period of history. The smelting of iron began in 1701 at the Kamensk and Nevyansk Works, and during the following years more than 20 iron refining and 60 copper smelting furnaces were built. Russia led the world in copper production in the first half of the 19th century. The Russian cast-iron and iron industry was of world-historical importance, and it had a considerable effect on the industrial revolution in England. The development of industry in Russia was based on the accumulated experience of centuries.

The speaker showed that Lomonosov took the first place in the creation of the scientific fundaments of metallurgy. He wrote in 1755: "...the openings of the interior of the earth...from them pour metals, which are plentifully distributed not only throughout our native land, but also to foreign nations. The heroic Russian army directs against the enemy weapons forged from Russian minerals by Russian hands".

Lomonosov's work "Fundamentals of metallurgy for ore workers", published by the Academy of Sciences in 1763, laid the scientific foundations of a number of geological, mining and metallurgical disciplines. The book received a wide circulation, and for over a century and a half it served as a practical manual for workers in the metallurgical industry. In contra-distinction to his other scientific works, which were not understood or appreciated by his contemporaries, Lomonosov was rewarded for this book by a special edict of the Empress Catherine II, his salary as a Civil Councillor being raised to 1875 roubles per annum.

According to Lomonosov theory and practice must constantly be correlated. "From observation to establish theory, through theory to put observation on the right track — this is the best of all ways of seeking the truth". He wrote that "a chemist should not be the sort of person who has gained his knowledge from the study of books only, he should have convinced himself by his own efforts of the truth of this knowledge", but at the same time he warns the student against an attitude of primitive empiricism.

Lomonosov's way of presentation was that of a real scientist, who works with a definite end in view, who does not lose sight of this end, and who maintains a rigorous scientific discipline in his thinking. Lomonosov's book, in which he presents the system of Russian scientific chemical terminology created by him, is one of the most remarkable books in the history of metallurgy, chemistry, and mining, for the novel and orderly way in which it is written.

In 1777, however, 12 years after Lomonosov's death, a slanderous anonymous article was published, announcing that this book was in fact only a translation of a book written by the director of the Nieder Hartz Metallurgical Works, one Schluetter; later historians of science (Academician V. I. Vernadsky, 1900) showed that these books have nothing in common. Schluetter's book contains 612 + 198 pages and 58 Tables, and it describes metallurgical practice in the Works under his control, whereas Lomonosov's book consists of 12 + 416 pages and 7 Tables, and it expounds the essentials of metallurgical industry, and also gives practical instructions. He shows in the preface how certain authors had uncritically copied information on the preparation of ores from other works, and he gives in his book a unitary system of metallurgical procedure.

I. N. Plaksin concluded with a description of the contributions made by Russian metallurgical chemists to the science of metallurgy, which were particularly numerous during the Stalin Five Year Plans.

Corresponding Member of the Academy of Sciences K. A. Kocheshkov presented to a meeting of the Division of Chemical Sciences of the Academy a paper written jointly with Candidate of Chemical Sciences E. M. Panov on "A new class of simple organic compounds of lead", on the 28th of November, 1951. The speaker reported that they had synthesized 7 representatives of a new class of metallo-organic compounds of elements of the IV Group of the periodic system, of the general formula $ArPbX_5$, by a very simple method.

Salts of lead organic acids were taken for the syntheses, which gave many advantages. The paper gave a detailed description of the new class, presented evidence of the structure of the compounds, and described a number of reactions given by them. It was shown for the first time that the reaction of dearylation of compounds of the class Ar_4Pb may proceed with elimination of three radicals, to give lead organic compounds in which lead is combined with only one aromatic radical.

The compounds of the new class give the usual reactions of lead organic salts. Addition of dilute alkalis or of aqueous ammonia to alcoholic solutions of phenyl-lead triisobutyrate gives a precipitate of the hitherto unknown phenylplumbic acid. The authors synthesized 5 new compounds of the class Ar_2PbX_2, and physical constants were determined for 3 of them. Lead organic compounds of the p-tolyl series of the class $ArPbX_3$ were synthesized.

Corresponding Member of the Academy of Sciences V. I. Spitsyn read a joint paper with L. D. Kolli, entitled: "Study of the processes of dehydration and thermal decomposition of certain heteropoly-compounds". These compounds are distinguished by a high water content, and little is known of the way in which this is bound. The paper reports the results obtained using a modified MacBain balance for the process of isobaric dehydration of lithium, potassium, and calcium silicotungstate and of potassium phosphotungstate and phosphomolybdate, at 25–500°. The results showed that in heteropoly-compounds containing phosphorus residual water is held much more firmly than in the case of those containing silicon. Replacement of potassium by lithium or calcium, the ions of which have a more powerful polarizing action, leads to weakening of binding of water. The amount of residual, most firmly bound, water in the silicon compounds studied is 0.5 mol, and in the phosphorus compounds 1 mol per atom of complex forming element. This effect corresponds to 1 or 2 hydrogen atoms being in a special position in the coordination structure, possible in the complex nucleus of the compounds.

The action of water on the residues obtained by calcination of the heteropoly-compounds was also studied. Lithium silicotungstate gives an insoluble residue when heated at 200°. Potassium and calcium silicotungstates are partially decomposed at 300°, and sodium phosphotungstate is decomposed only at more than 300°.

The aqueous extracts and the calcined residues were analyzed. Thermal decomposition of alkali metal salts of silicon-containing heteropoly-compounds gives a soluble silicate, and not silica, whereas phorphorus-containing compounds yield soluble alkali metal phosphates under these conditions. It is evident that these reactions result from an appropriate position of the silicon, and also of the phosphorus, atoms in the compounds, and it is very probable that the position of silicon or phosphorus in the coordination nucleus of the heteropoly-compounds in relation to the cation of the outer sphere is to a certain extent approached to that of tungsten and molybdenum.

AWARD OF D. I. MENDELEEV PRIZES FOR 1951

The Praesidium of the Academy of Sciences USSR has awarded D. I. Mendeleev prizes for 1951, for the following work:

Prizes of Rb. 20,000 each

1. To Doctor of Chemical Sciences A. V. Kirsanov for his series of papers "Researches on the transformation of sulfanilic acid, and syntheses performed with sulfanilamide".

2. To Candidate of Physico-Mathematical Sciences Yu. N. Ryabinin for his paper "On certain properties of dense gases".

Prizes of Rb. 10,000 each

1. To Doctor of Chemical Sciences A. V. Kiselev for his paper "Structure of adsorbents and energy of adsorption".

2. To Doctor of Chemical Sciences A. I. Shatenshtein for his papers "Theory of acids and bases", "Comparison of the strength of very weak acids", and "Studies of isotope exchange in liquid deutero-ammonia".

A. V. Kirsanov's series of papers on the reaction between sulfanilic acid and phosphorus pentachloride, and on the study of the properties of trichlorophosphazosulfuryl chloride formed therefrom, is an orginal and productive research. He showed that previous workers had been mistaken, and that the product was in reality the chloride of trichlorophosphazosulfuric acid, and not a complex of sulfanilic acid with phosphorus trichloride, as had been believed before. Kirsanov establis' ed the structure proposed by him by means of scrupulous analyses and by study of its properties.

A. V. Kirsanov extended the reaction discovered by him to the study of the reaction of arylsulfanilamides with phosphorus pentachloride, and found that the products are trichlorophosphazosulfonaryls; the structures suggested for these products by earlier workers are mistaken. Kirsanov studied the reaction of thermal decomposition of the chloride of trichlorophosphazosulfuric acid, with the object of obtaining an interesting product, viz., that obtained by elimination of PCl. A series of trimers of this product were obtained, and it was named sulfanuryl chloride, by analogy with cyanuryl chloride. Kirsanov then presented the results of research on the so-called imidosulfanilamide (hydrolysis, methylation, etc.), leading to the elucidation of its structure and properties. One of the interesting applications of the reaction described by Kirsanov is his new method for preparation of nitriles of carboxylic acids by the use of trichlorophosphazosulfonearyls.

Kirsanov's work is of a high scientific level, and was done with much skill.

Yu. N. Ryabinin's paper "On certain properties of dense gases" is an experimental study of the properties of certain gases (air, nitrogen, argon) adiabatically compressed at pressures of the order of tens of thousands of atmospheres. He was able to perfect known methods of adiabatically compressing gases at these ultra-high pressures, and he describes a reliably working equipment for the study of gases at pressures of 10,000 atmospheres and at temperatures of about 9000° attained during adiabatic compression. This apparatus permitted of the measurement of the volume and pressure of adiabatically compressed gases, of the study of their optical properties, of the measurement of their electrical conductivities and of the study of chemical reactions (oxidation of nitrogen) taking place in adiabatically compressed air. The author found that at high pressures distribution of energy at different frequencies follows Wien's law. This made it possible to determine the temperature of the compressed gases.

Electroconductivity measurements showed that adiabatically compressed air is ionized, and is therefore a super-dense plasma. It was shown that at voltages of 30-17, 800 V/cm the electroconductivity of the gas is of an ohmic nature. It was also found that in gases of very high density the ionization potential is lowered in comparison to that of an isolated atom, and an explanation of this phenomenon is given. Ryabinin found further that the adiabatically compressed gases obey the ideal gas equation. Although this finding is not an unexpected one, in view of the very high temperature developed during the adiabatic compression of gases, Ryabinin was the first to confirm this quantitatively.

His studies of the oxidation of nitrogen during adaiabatic compression of air are of considerable scientific importance. Ryabinin's work has resulted in the opening up in the USSR of a new domain of study — that of physical and chemical phenomena in adiabatically compressed gases. These important studies have contributed to the extension of our knowledge of the condensed state of matter. Thanks to them world scientific literature has for the first time received information on the properties of gases at super-high pressures and at very high temperatures.

A. V. Kiselev's paper "Structure of adsorbents and energy of adsorption" is an outstanding experimental and theoretical study, being a striking concrete example of the superiority of Soviet over foreign science. The original theoretical parts of the paper are those concerning an adsorptional-structural method of study of highly disperse and porous bodies, with, as a general conclusion, the concept of structural types of adsorbents. Of considerable importance is the theoretical analysis of the effect of adsorbent structure on the shape of the isotherms, and also of the stratification taking place in the gaseous or liquid phase in contact with the adsorbent. The new phenomenon of capillary stratification in adsorption from solutions was not only predicted theoretically but was also demonstrated experimentally, and was studied in detail. There is also much original thought in the "thermodynamics of adsorptional processes" developed by the author.

One of the most important of Kiselev's experimental achievements is the design of a precision adsorptional calorimeter with constant heat exchange, and with a temperature sensitivity substantially exceeding that of any known calorimetric apparatus. A very broad and systematic survey was made of different adsorbents belonging to various structural types, and it yielded quite important results. Absolute values for adsorption and for energy of adsorption, both per unit area of adsorbent, were for the first time measured and compared for porous and non-porous adsorbents. Of considerable theoretical and practical significance are the researches on poisoning and regeneration of silica gel surfaces in adsorption of methanol, shown to be due to formation of surface ethers.

The systematic application of the adsorptional-structural method to the most diverse adsorbents led to the obtaining of very valuable results, of immediate practical applicability. A detailed analysis of the processes of multimolecular adsorption and of capillary condensation was made, on the basis of the experimental results for the adsorption isotherms and the differential heat of adsorption.

A. L. Shatenshtein's monograph "Theory of acids and bases" presents the history of the development of the theory of acids and bases, and gives a detailed critical review of contemporary theories. The outstanding role played by Russian scientists in the development of the progressive theoretical treatment of the subject is shown.

The evaluation and criticism of contemporary theories are based largely on the experimental work of the author, consisting of studies of solutions in non-aqueous solvents, chiefly liquid ammonia and sulfur dioxide; the most important results of this work are given in a summarized form in the monograph.

The author gives a comprehensive picture of acid-base equilibria in liquid ammonia, this being of fundamental importance for the theory of protolytic acid-base equilibrium, since liquid ammonia is one of the most protophilic solvents known. Differences between the strengths of strong acids disappear in liquid ammonia, and the strength of weak acids rises sharply, thus making it possible to compare the acidity of substances which do not display acidic properties in aqueous solution.

The results obtained are also of interest for the theories of solutions and of homogeneous catalysis, since they include the first quantitative data obtained for acid catalysis and for salt effect in liquid ammonia. Owing to the low dielectric constant of the solvent, ionic association takes place in even quite dilute solutions, and the velocity and energy of activation of the reaction of ammoniolysis depend not only on the charge but also on the radius of ions of acids and salts present in the solutions.

The researches on solutions in liquid sulfur dioxide allowed the author to formulate a concept of aprotonic, acid-like substances which can, similarly to acids, take part in equilibria with bases.

The study of weak acids was continued in the paper "Comparison of the strength of very weak acids", the results of which were presented in a more detailed form in the article "Researches on reactions of isotope exchange of hydrogen in liquid deutero-ammonia". The measurement of the velocity of exchange reactions of hydrogen isotopes in this medium is suggested as a quantitative method for comparison of the lability of hydrogen in different hydrocarbons. The importance of this method extends beyond the limits of the theory of acids and bases; it opens the way towards the achievement of new results of interest to theoretical organic chemistry.

The work of A. L. Shatenshtein is an important contribution to the theory of acids and bases, as well as to the theory of reactivity of organic compounds. It opens up wide perspectives for the making of further generalizations, and for the obtaining of new data of importance to theoretical organic chemistry.